NEW UPGRADING TECHNOLOGIES APPLICABLE TO HEAVY OIL AND BITUMEN

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by:

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LIST OF ABBREVIATIONS, ACRONYMS AND TERMS

AOSTRA Alberta Oil Sands Technology & Research Authority

Bbl Barrel (42 US Gallons)
BPSD Barrels per Stream Day
BS&W Basic Sediment and Water

CCR Conradson Carbon Residue – Measure of Coking Tendency

cPs Centipoise (Viscosity Measure)
CRC Cold Radiation Cracking
cSt Centistoke (Viscosity Measure)

DAO
Deasphalted Oil (Light Product from Solvent Deasphalting)
DilBit
Bitumen Diluted with C₅ Condensate to Meet a Viscosity Spec

EPC Engineering, Procurement and Design

FBC Fluidized Bed Combustor FCC Fluid Catalytic Cracking

FT Fischer Tropsch

HDN Hydrodenitrification (Nitrogen Removal)
HDS Hydrodesulfurization (Sulfur Removal)

IPO Initial Price Offering

KBPSD Thousands of Barrels per Stream Day

KGy Kilo Gray – Unit of Radiation

LCO Light Cycle Oil (Diesel Product from FCC Process)

LOI Letter of Intent

MM Millions

MOU Memorandum of Understanding
MPa Mega Pascal (Measure of Pressure)

MT Metric Ton NA North America

NCUT National Center for Upgrading Technology (Canada)

NRC National Resources Canada

POX Partial Oxidation

RFCC Residue Fluid Catalytic Cracking SAGD Steam Assisted Gravity Drainage

SCF Standard Cubic Feet (Measured at 60°F, 14.7 psi)

SCO Synthetic Crude Oil

SDA Solvent Deasphalter – Separates Resid - Asphaltenes and DAO SMR Steam Methane Reforming – Process for Hydrogen Production

SOR Start of Run

SynBit Bitumen Diluted with SCO to Meet a Viscosity Specification

TAN Total Acid Number
TC Thermal Cracking
TPD Tons per Day (Metric)
VGO Vacuum Gas Oil

Wppm Weight Parts per Million WTI West Texas Intermediate

EXECUTIVE SUMMARY

An analysis of twenty-four (24) new technologies which have been developed for the upgrading of heavy oil and bitumen is discussed in this study report. The focus of the study is technologies developed primarily for the upgrading of heavy feedstocks from Western Canada. Sixteen (16) of the processes are considered partial upgrading with many having been developed in the past few years. Partial upgrading of heavy oil and bitumen is not currently commercialized. As a result of high oil prices, fluctuations in the light to heavy oil price differential, limited capital, and the development of promising new technologies, partial upgrading is expected to be implemented in the near future. Eight (8) of the processes investigated are full upgrading (no vacuum residue in SCO product) and are also relatively new technologies with some commercialized or with a commercial plant under construction.

Based on published information and, for some technologies, discussions and visits with the licensor, a technical analysis of each process was performed. This analysis resulted in the development of information and subjective opinions, which can allow the study recipient to understand the key features and to consider the merits and deficiencies for each process.

For each technology, a process description, process objective, patents, R&D capabilities, strength and weaknesses, current status, preferred applications and a summary were developed. Also included is a subjective analysis of the process claims and technical and economic merits of the technology. *Attachments 1 and 2* are hyperlinked lists of important references and patent and patent applications which can be utilized to further study a technology and to evaluate the developer or licensors' capabilities.

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A summary of the important findings for the partial upgrading technologies is shown in *Table 1* (two pages). Only one of the sixteen processes (Sonocracking) has been commercially demonstrated although the probability of the licensing of this technology in North America with a heavy oil feed is nil. The H-Oil Process is a commercial technology although not in the partial upgrading mode. A commercial Value Creation Technology plant initiated construction in 2006 although construction was suspended and the project is now cancelled. All others processes are years away from constructing a commercial plant.

Most of the partial upgrading processes studied are thermal in nature and do not utilize a catalyst or require hydrogen. Only the H-Oil and the Wildcatter HCU Processes are hydrogen addition technologies. In the case of the Wildcatter HCU, the hydrogen is generated from the coke formed in the thermal cracking step. The thermal conversion of the vacuum residue in the heavy oil feedstock is accomplished via a variety of methods including mild thermal cracking, coking, sound energy, high energy electrons, and kinetic energy associated with a high pressure drop nozzle/orifice. The estimated SCO yield for the thermally-oriented partial upgrading processes which can produce a transportable SCO is typically in the range of 70-75 V%. The unconverted residue, asphaltenes or coke produced is typically combusted to generate steam for a SAGD Project.

Twelve of the sixteen processes are currently considered to be at a moderate or high level of activity including pilot plant evaluations, demonstration plant operation and active marketing. It is concluded that eight of the sixteen processes can produce a transportable SCO from Western Canadian heavy oils or bitumens and completely eliminate diluent blending. Four processes will reduce but not eliminate diluent requirements and for four processes it is currently unknown if a transportable SCO can be created. Five of the new technologies are judged to

have a moderate to high probability of eventual commercialization in North America. These are the CPJ, HTL, H-Oil, IYQ, and Value Creation technologies.

A summary of the study findings for the eight new full upgrading technologies is shown in *Table 2*. The Opti Canada OrCrude Process was commercialized in early 2009 at the Long Lake Project; however as of May 2010 the Long Lake facility has only attained approximately ¼ of full feedrate capacity. With a relatively low SCO yield and the requirement of large and costly gasifiers, additional OrCrude Process commercial plants are not expected in the short-term. The Genoil Process is judged to be an inferior process, with low technical merits and nil chance of being commercialized in North America. The Chattanooga Process is unique in that the feedstock is the mined tar sands, not the extracted bitumen. This process is in the initial phases of development, is fairly complex, and is estimated to have high investment and operating costs. However, with the elimination of the extraction and froth treatment facilities and the tailings pond, it may be economically attractive.

The EST, HCAT, HRH, Uniflex and VRSH technologies are similar slurry catalyst processes which operate at high residue conversion and typically combust the small remaining quantity of vacuum residue. The EST Process, which includes solvent deasphalting of the unconverted residue and inclusion of the DAO in the SCO, will be commercialized in late 2012 with a plant under construction at an Eni affiliate refinery. Of the remaining slurry catalyst technologies (HCAT, HRH, Uniflex and VRSH), the Chevron VRSH and the UOP Uniflex Processes are judged to have the highest chance of North American commercialization given the licensors' reputation and in the case of Chevron, imminent plans for a large-scale (3,600 BPD) demonstration plant.

Table 1
<u>Summary of Partial Upgrading Processes</u>

Process	Aqua- conversion	CCU ¹	<u>СРЈ</u>	EADIEMAC	HTL	<u>H-Oil</u>	Ī _A Ō	<u>JetShear</u>
Licensor	UOP & FW	UOP	Wesco Energy	Eadie Oil	Ivanhoe Energy	Axens NA	ETX Systems	Fractal Systems
Type of Process	Catalytic Visbreaking	1 - RFCC 2 - SDA+ RFCC+FBC	Thermal Cracking	Froth Treat. Visbreaking	Pyrolysis + Coking + Combust	Ebullated- Bed	Coking+ Combust	Thermal Cracking
Catalyst / Hydrogen Utilized	Yes / No	Yes / No	No / No	No / No	No / No	Yes / Yes	No / No	No / No
Disposition of Unconverted Residue	SCO	Combust/ SCO	Combust/ SCO	SCO	Combust/ SCO	SCO	Combust/ SCO	Combust/ SCO
Estimated SCO Yield, V%	~100	70 - 80	75 – 85	~100	75 - 85	100+	80 - 90	UN
Significant Export Steam	No	Yes	Yes	No	Yes	No	Yes	UN
Commercialized	Test	No	No	No	No	No	No	No
Demonstration Plant	No	No	Yes	No	Yes	Yes	No	No
Patents or Applications Found	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes
Level of Current Activity	Low	Mod/Low	Low	Low	High	Mod	High	Mod
Produce Transportable SCO from Bitumen	No	Yes	Yes	No	Yes	Yes	Yes	No
Additional Development Required	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes
Probability of Commercialization in NA	Low	Low	Mod	Nil	High	Mod	Mod/High	Low

Table 1 (Continued) <u>Summary of Partial Upgrading Processes</u>

Process	Petro <u>Beam</u>	PetroSonic	Sono- cracking	TRU	Value <u>Creation</u>	VISCOSITOR	Wildcatter <u>HCU</u>	WRITE
Licensor	PetroBeam	Sonic Technology Solutions	SulphCo	TRU Oiltech	Value Creation	Ellycrack	Refinery Science	Western Research Institute
Type of Process	High Energy Electron Cracking	Thermal Cracking +SDA	Thermal Cracking Via Sound	Thermal Cracking + Reagent	Deasphalting +Coking+ Combustion	Pyrolysis + Coking + Combustion	Catalytic Thermal Crack + FT	Coking
Catalyst / Hydrogen Utilized	No / No	Yes / No	Yes / No	Yes / No	No / No	No / No	Yes / Yes	No / No^3
Disposition of Unconverted Residue	SCO	Combust/ SCO	SCO	Combust/ SCO	SCO	Combust/ SCO	Gasify/ SCO	Coke
Estimated SCO Yield, V%	UN	80 - 90	~100	75 – 85	75 – 85	75 – 85	UN	70 - 85
Significant Export Steam	No	Yes	No	Yes	Yes	Yes	Yes	UN
Commercialized	No	No	Yes	No	No	No	No	No
Demonstration Plant	SU	No	Yes	No	UN	No	No	No
Patent or Applications Filed	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
Level of Current Activity	High	Mod/High	Mod	Mod	Low/Mod	Low	Low	Low/Mod
Produce Transportable SCO from Bitumen	UN	Yes	No	Un	Yes	Yes	UN	UN
Additional Development Required	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
Probability of Commercialization in NA	Low	Low/Mod	Nil	Low	Mod	Low/Mod	Low	Low

- 1. Two Process Versions are Available
- 2. UC = Under Construction / SU = In Start-up / UN = Unknown
- 3. Hydrotreatment of Light Products may be Required

Table 2
<u>Summary of New Full Upgrading Processes</u>

Process	Chattanooga	<u>Genoil</u>	<u>EST</u>	<u>HCAT</u>	<u>HRH</u>	<u>OrCrude</u>	<u>Uniflex</u>	<u>VRSH</u>
Licensor	Chattanooga	Genoil	Eni S.p.A.	Headwaters	MobisEnergy ¹	Opti Canada	UOP	Chevron
Type of Process	Fluidized-Bed	Fixed-Bed	Entrained-Bed + SDA	Entrained-Bed	Entrained-Bed	SDA + TC + Gasification	Entrained Bed	Entrained or Ebullated-Bed
Type of Catalyst	Optional	Extrudate	Slurry	Slurry	Slurry	None ²	Slurry	Slurry
Hydrogen Required	Yes	Yes	Yes	Yes	Yes	No ²	Yes	Yes
Typical Residue Conversion, %	90+	UN	80 - 85	80 - 95	90 - 100	<80	80 - 95	90 - 100
Preferred Feedstock	Mined Oil Sands	Heavy Oil or Bitumen	Heavy Oil or Bitumen	Heavy Oil or Bitumen	Heavy Oil or Bitumen	SAGD Bitumen	Heavy Oil or Bitumen	Heavy Oil or Bitumen
Disposition of Unconverted Residue	Coke Purge	UN	DAO to SCO Asphaltene- UN	Combustion or Gasification	Combustion	Gasification	Combustion or Gasification	Combustion
Commercialized	No	No	UC	No	No	Yes	No	No
Demonstration Plant	No	No	Yes	No	Yes	Yes	Yes – CANMET	Designed
Level of Current Activity	Low	Mod	High	Low	Mod	High	High	Mod/High
Additional Development Required	Yes	Yes	No	Yes	UN	No	Yes	Yes
Probability of Commercialization in NA	Low	Nil	Mod	Low/Mod	Low	-	Mod	Mod

^{1.} Licensing the Process in North America

^{2.} Although not a Part of the OrCrude Process, a High-Pressure Catalytic Hydrocracker is fed the TC and Straight Run Distillates and VGO

^{3.} UN = Unknown / UC = Under Construction

INTRODUCTION

Heavy oil upgrading involves the processing of heavy crude or bitumen using refining operations including distillation, coking, thermal cracking, catalytic cracking, catalytic hydrocracking, solvent deasphalting and gasification. To effectively upgrade these heavy oils, it is necessary to convert a portion of the heaviest portion of the oil (vacuum residue) to lighter boiling components.

Heavy oil upgrading technologies can be segregated into full and partial techniques. Currently, only full upgrading is practiced in Western Canada, the location which is the focus of this study. In the near future, both upgrading techniques are expected to be utilized to produce transportable, light synthetic crude oil (SCO) of varying quality. The SCO is typically transported to refineries in North America (eventually in Asia) where final refining is carried out to produce saleable petroleum products.

Full Upgrading

In general, full upgrading produces either finished saleable products or an SCO which is completely void of vacuum residue. All the SCO would distill below approximately 1000°F. Typically, the SCO distillation products are hydrotreated and of high quality at or near that required for final sales. Most of the worldwide activity in heavy oil upgrading/conversion is in Western Canada where there is a vast quantity of heavy oil reserves including bitumen from oil sands. The current Upgraders in Western Canada are all full upgrading facilities and produce a bottomless (i.e., no vacuum residue) SCO product. The SCO is either transported to North America refineries for final refining or it is used as a diluent where it is blended with heavy oil or bitumen to produce a transportable SynBit.

Eight new full upgrading technologies are investigated in this study include: 1) a process (*OrCrude*) incorporating SDA, DAO thermal cracking, and gasification, 2) a fluidized-bed process (*Chattanooga*) which operates on the mined tar sands, not the extracted bitumen, 3) a new "enhanced" fixed-bed process (*Genoil*), and 4) five slurry catalyst processes (*EST*, *HCAT*, *HRH*, *Uniflex and VRSH*) all targeting high conversion. The OrCrude Process was recently commercialized with the early 2009 start-up of the Long Lake Project. The Eni EST Process is scheduled to be commercialized in late 2012 with a 20,000 BPSD plant under construction at an Eni affiliate refinery in Italy.

Partial Upgrading

Partial upgrading produces an SCO which typically contains 5-30% vacuum residue and distillation products which require additional refining (hydrotreating). Many partial upgrading process configurations are targeting the production of SCO just meeting the pipeline specifications for gravity and viscosity (i.e., is pumpable). Typically this requires a minimum API gravity of 19°, a maximum 7°C viscosity of 350 cSt and a BS&W sediment less than 0.5 V%. Acceptable partially upgraded SCO will not require dilution with natural gas condensate or other lighter oils to be transported via pipeline. Many of the new partial upgrading technologies investigated in this study were developed to also produce significant excess energy (steam) which can be utilized for resource acquisition (SAGD).

Many of the new partial upgrading technologies include two steps, a low-investment thermal cracking of the vacuum residue followed by combustion of the heavy unconverted product, which is typically coke. The combustion of the coke or heavy unconverted product (residue, asphaltenes) can produce the steam needed for the process and all or a portion of that required for SAGD. The thermal cracking of the

residue is accomplished by various techniques including the use of heat, sound energy, kinetic energy and irradiation. In some of the new partial upgrading processes, catalytic cracking is utilized. Since the catalyst cost for partial upgrading can be prohibitive, development efforts have included the use of an inexpensive, recyclable catalytic material.

Besides the lack of commercial experience, the largest issues concerning the implementation of the partial upgrading of heavy oil are:

- 1. The Stability and Compatibility of the SCO Product As discussed above, many of the new processes utilize thermal cracking to convert all or a portion of the vacuum residue in the feedstock. Thermally cracked materials tend to be unstable and can form solids when combined with other pipeline or refinery streams. Many of the new partial upgrading processes include technology features which claim to minimize the instability of the product relative to delayed coking. These include lower operating temperatures, short reactor residence times, near complete conversion, and separation of the feedstock asphaltenes. Stability and compatibility testing of the final SCO is required to confirm these claims.
- 2. <u>The Value of SCO Product</u> Typical partially upgraded SCO has a low API gravity (~20°), fairly high sulfur and relatively low vacuum residue content. There is no current commercially sold SCO with similar inspections; the closest analog is DilBit based on Cold Lake and Lloydminster heavy oils. These DilBits however, have much higher vacuum residue contents than partially upgraded SCO and historically sell at approximately 25% discount to WTI. Licensors of the new partial upgrading processes have estimated discounts (below WTI) for their SCO in the range of 0 to 20% based in part on the benefit

of low vacuum residue content. The economic viability of a partial upgrading route is highly dependent on the price received for the SCO product and discounts of 10-15% (below WTI) are typically required.

Current Trends

As a result of recent high oil prices and oil sands development in Western Canada, the development of techniques and processes for the full and partial upgrading of heavy oil and bitumen has been active, particularly in the past few years. In many cases these technologies have been initially developed for other applications and modified for application to the heavy oil and bitumen feedstocks. As an independent technology expert, Consultant has previously evaluated many of the new technologies including discussions with key personal and pilot plant visits. Some of the processes are in the initial development stage while others are commercialized or commercialization. Given the high level of interest in the development of oil sands and heavy oil projects, a great deal of media and investor attention is paid to new processes, particularly those which claim great technical and economic breakthroughs.

The study report will result in recipients being aware of the direction of the heavy oil upgrading field and being able to sort through the numerous press releases and frequent incredible claims. The primary study objective was to identify those technologies which merit further study and investigation.

This report also includes a summary of the mature primary technologies which are currently utilized in Western Canada (coking and ebullated-bed hydrocracking) and a discussion of coke/residue gasification. This is provided in the next section.

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SUMMARY OF EXISTING COMMERCIAL PROCESSES

This Colyar Consultants study report examines new partial and full upgrading

technologies which are applicable for processing heavy oils and bitumen. With a few

exceptions, most of these new technologies investigated in the current study have not

been commercialized. In Western Canada, all but one of the currently operating

Upgraders or those under construction have utilized well-established coking (delayed

and fluid) and ebullated-bed processes for conversion of the vacuum residue in the

heavy oil or bitumen. For two of the currently operating Upgraders (Syncrude Canada

and Husky Energy), both ebullated-bed hydrocracking and coking are utilized with the

unconverted vacuum residue from the ebullated-bed process routed to the coker.

As part of any evaluation process, the new partial upgrading and full upgrading

technologies may be eventually judged against the existing commercial technologies

discussed above. To have an appreciation for these existing processing routes,

summary information on coking and ebullated-bed processing is provided below. Also

included is a discussion of residue/coke gasification which is becoming more

important and has been implemented in Western Canada with the start-up of the Long

Lake Project in early 2009.

Coking

By far, coking is the most prevalent conversion technique. Worldwide, there are over

100 delayed coking installations processing over 4 MM BPCD of heavy feedstock

with 50 MM TPY of coke production. The majority of cokers are the delayed type

with over one-half of the units located in North America.

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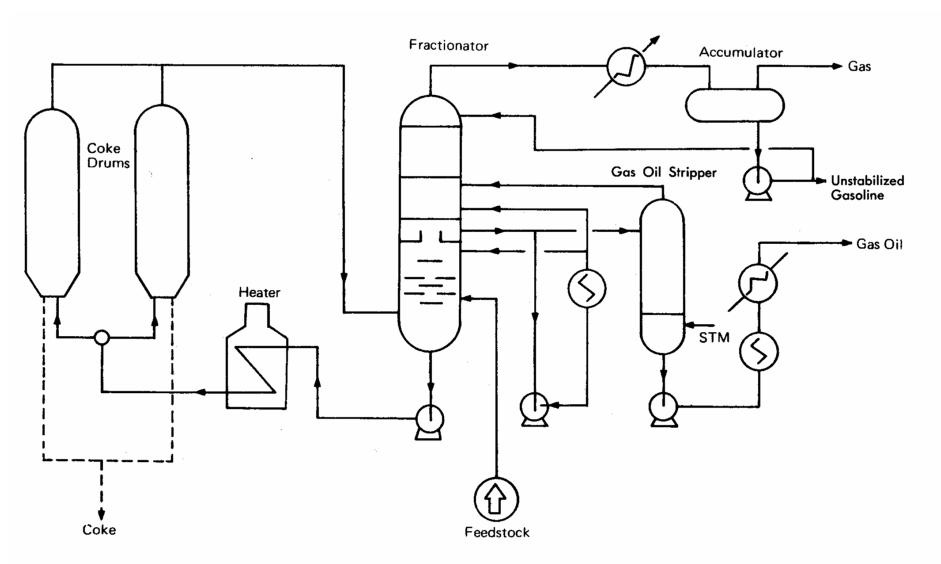
In Western Canada, cokers are employed in the Suncor (delayed), Syncrude Canada (fluid), Husky Lloydminster (delayed), and the recently started-up CNRL (delayed) Upgraders. Cokers are also planned for many of the upgraders under design.

The overall delayed coking processing scheme is shown in *Figure 1*. The coker feedstock is fed to the bottom of the coke fractionator along with recycled oil. The combined feed is pumped to the coker furnace where it is exposed to cracking temperatures at short residence time. The residence time is sufficiently short such that minimal coking takes place in the furnace and the liquid is sent to the coke drums where the cracking actually occurs. Parallel coke drums are typically provided with one drum on-line and the other off-line for coke removal. The overhead from the drums enters the fractionator and is separated into naphtha, diesel and gas oil products.

The delayed coker operates at low pressure and 800-850°F and produces light gases, liquids boiling up to approximately 975°F and a solid coke product. Coker liquids are hydrogen deficient and aromatic with relatively high heteroatom contents. The coke yield is typically 1.3 to 1.7 times the weight of the CCR (Conradson Carbon Residue) in the residue feedstock.

Fluid coking uses a circulating fluidized-bed reactor where the formed coke particles are the media which is fluidized. The vacuum residue feed is sprayed onto the high temperature coke particles where the cracking reactions occur and coke is laid down. The coke is circulated to a fluidized-bed boiler where a portion is burned off using air. The heated coke particles are then re-circulated to the feed reaction vessel. The primary advantage of fluid coking is lower net coke yield. Flexicoking is an extension of fluid coking where the coke is gasified with air to produce a low-BTU syngas. There are approximately 15 fluid and Flexicokers worldwide.

Figure 1 **Delayed Coker Flow Diagram**



Ebullated-Bed Hydrocracking

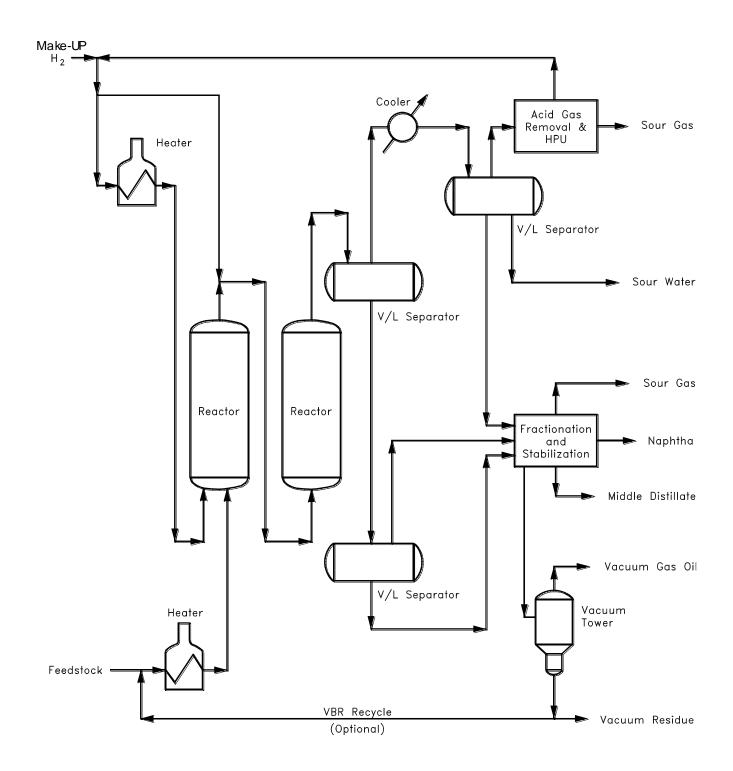
The ebullated-bed reactor is a commercial fluidized-bed, three phase system with back-mixing of both the reactor liquid composition and the catalyst particles. The catalyst used in the ebullated-bed is held in a fluidized state through the upward lift of liquid reactants (feed oil plus recycle) and gas (hydrogen feed and recycle) that enter the reactor plenum and are distributed across the bed through a distributor and a grid plate. The height of the ebullated catalyst bed is controlled by the rate of recycle liquid. This liquid rate is adjusted by varying the speed of the ebullating pump, which varies the flow of ebullating liquid obtained from the internal vapor/liquid separator normally located inside the reactor. Operation in this ebullated state results in low reactor pressure drop, and a back-mixed, nearly isothermal bed. Fresh catalyst can be added and spent catalyst withdrawn to control the level of catalyst activity (i.e., desulfurization) in the reactor. capability of the daily addition of a small quantity of catalyst is a key feature of the ebullated-bed reactor and results in constant product quality over time. The run length for the ebullated-bed reactor system is therefore not a function of catalyst activity, as in a fixed-bed system. To adjust for different feedstocks or levels of desired product quality, the rate of catalyst replacement or the type of catalyst utilized can also be changed without shutting down the reactor.

Ebullated-bed technology for vacuum residue conversion/upgrading is licensed by Axens (H-Oil_{RC}) and Lummus Crest (LC-Fining). There are more than 15 commercial units operating at residue conversion levels of 40 to 75%. Three of the units are in Western Canada (Husky, Syncrude Canada, and Shell Canada). The ebullated-bed reactor is well suited for the processing vacuum residue feedstocks containing high metal, CCR and asphaltene contents. Reactor operating conditions are temperatures of 770-830°F and total pressures of 2,000-

3,000 psi. Problems/issues with ebullated-bed technology include a high investment cost, requirement of a high degree of operator expertise, high annual catalyst cost, and possible sediment formation (fouling) as the residue conversion is increased.

The H-Oil_{DC} Process is an ebullated-bed hydrotreating / hydroconversion process for treating distillates, vacuum gas oils and DAO. The process is an extension of the commercially demonstrated H-Oil_{RC} Process which operates on vacuum or atmospheric residues. The H-Oil_{DC} operating temperature is similar to H-Oil_{RC} / LC-Fining. Pressure is adjusted for the specific feedstock and the required level of severity. H-Oil_{DC} Process feedstocks include vacuum gas oils containing significant quantities of contaminant metals, CCR or solids and DAO's. These feeds would be difficult for a fixed-bed reactor and would eventually result in bed plugging or a short catalyst cycle time. The first commercial H-Oil_{DC} Unit is located in Perm Russia and processes a mixture of Russian VGO's at 20 - 50% conversion. For the conversion/upgrading of a DAO with low/nil asphaltene content, the H-Oil_{DC} Process can be operated at 75-90% residue conversion and result in good distillate and VGO product qualities.

Figure 2
Ebullated-Bed Flow Diagram



The Role of Gasification

Gasification is a non-catalytic process for the production of a syngas from any hydrocarbon stream. Primary licensors are Lurgi, Shell and Texaco. The reactions include pyrolysis, partial oxidation and steam gasification and typically occur in a single moderate pressure, high temperature (>2,000°F) reactor. Reactor feeds include the hydrocarbon, steam and oxygen. The syngas will contain CO, CO₂, H₂ and H₂O at a molar ratio dictated by equilibrium. The product gas will also contain H₂S, NH₃ and small amounts of COS and CH₄.

The syngas can be scrubbed, treated to remove H_2S , NH_3 and COS and used directly as a low BTU fuel gas. For the production of hydrogen, the cleaned syngas is reacted catalytically via the water gas shift reaction $H_2O + CO \leftrightarrow H_2 + CO_2$ with the objective of "shifting" the carbon monoxide to hydrogen. Any residual CO and CO_2 are reduced with hydrogen to produce methane (Methanation Step). The hydrogen product can be up to 98-99% pure. The large portion (~90%) of the CO_2 produced in gasification and shift can be recovered, purified, compressed, and sequestrated or used for enhanced oil recovery. Relative to traditional natural gas reforming (SMR) for hydrogen manufacture, a larger fraction of the CO_2 produced can be recovered in a gasification plant.

In the past, gasification was not seriously considered for Upgrader applications due to the availability and low cost of natural gas and also due to the high gasification investment cost. Gasification requires a high investment due to the large reactor utilized, severe operating conditions, equipment sparing/duplication, and the need for an oxygen plant. SMR has been the most prevalent and economical method for hydrogen production; however when natural gas prices are high or when natural gas is unavailable, gasification is preferred. Natural gas costs of approximately \$10/KSCF are typically required for gasification to be

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economically preferred.

Gasification and shifting followed by the Fisher-Tropsch (F-T) Process can be utilized to produce additional liquids from the coke, heavy residue or asphaltenes produced from primary conversion processes. This route will maximize the total liquids production from an Upgrader but will result in an extremely high investment cost. The addition of the F-T step to the gasification of Upgrader gasification is not economically feasible. One of the partial upgrading processes examined in this study (Wildcatter HCU) has specified this route for elimination of the coke product from a thermally cracking conversion process.

DISCUSSION FOR EACH PROCESS

In the following section, each new upgrading process is discussed. The sixteen

partial or field upgrading technologies are listed first in alphabetical order,

followed by the seven new full upgrading technologies.

Each process discussion includes a process description, objective, patents, R&D

capabilities, scale-up, strengths and weaknesses, current status, preferred

applications and a subjective technical summary. An effort has been made not to

be excessively technical but to focus on the overall technical and economic

feasibility and relative merit of the process concept. Also included is a subjective

analysis of the process claims and technical and economic merits of the

technology. When appropriate, comments on the capability of the current

technical staff and management to commercialize the technology are also

provided.

When viewing this document on a computer (PDF file), the internal

hyperlinks//bookmarks allows one to navigate throughout the document by a

simple click. Returning to the previous document location is accomplished by a

combination of the Alt and left arrow key or $\langle Alt \rangle \langle \leftarrow \rangle$.

As a result of a wide range of publically available information and the varying

stages of process development, the process discussions shown in this section will

emphasize different aspects of a technology. For commercial or near-commercial

processes, the discussion emphasis may be on current projects; for new, non-fully

developed processes, the discussion may focus on understanding the unique

technical merits and process claims.

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In all cases, a subjective technical assessment of the process is discussed. It is noted that this assessment is based on Consultant's technical knowledge and the currently available information. This assessment could possibly change after analyzing additional data or after initial or additional discussions with the process licensor.

The report includes two attachments which are instrumental for further studying and understanding the upgrading technologies. *Attachment 1* is a listing of important publications and news articles (primarily conference presentations and press releases). *Attachment 2* is a list of all key U.S. and Canadian patent and patent applications. For most of the publications and news items and for all the patent and patent applications, there are hyperlinks which can be opened and viewed on a computer.

Partial Upgrading Processes

Aquaconversion Process

by Foster Wheeler and UOP

Process Name: Aquaconversion Process Go To: Publications Patents

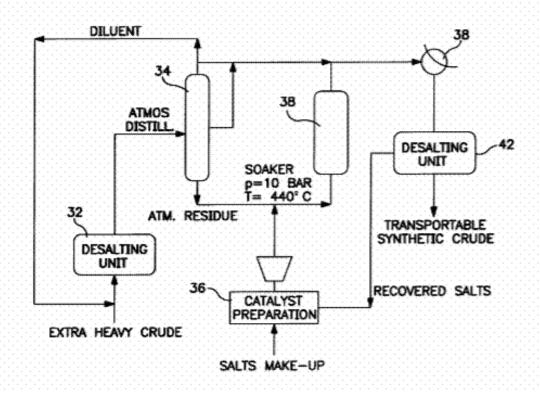
Companies: Developed by Intevep, (Venezuelan Government Controlled)

Licensed by Foster Wheeler and UOP

U.S. Public Companies

Website: http://www.fwc.com

Process Overview & Objective: The Aquaconversion Process is an enhanced visbreaking process which utilizes steam and a dual catalyst system to obtain relatively high conversion and improved vacuum residue quality. The process was invented in the mid 1990's by Inteven which is the technology arm of PDVSA, the national Venezuelan oil company. In 1997, Intevep, UOP, and Foster Wheeler signed a joint development and commercialization agreement for the advancement of the Aquaconversion Process. The basic process is similar to conventional soaker-type visbreaking. Existing visbreakers can be retrofitted to run in the Aquaconversion mode. The process was commercially demonstrated at the Isla refinery in Curacao in 1996/1997; however a dedicated commercial facility has yet to be constructed. The primary objective of the process is to enable deeper conversion and viscosity reduction of residues relative to traditional visbreaking while maintaining the heavy product stability. The major Aquaconversion claims are vacuum residue conversion as high as 50%, a 4-6°API increase in product gravity, and halving of the viscosity relative to typical visbreaking. The process was also termed SCSC (Selective Catalytic Steam Cracking) in a 2002 PDVSA publication.



A process flow diagram for the Aquaconversion Process for producing a transportable Orinoco SCO is shown above. Relative to traditional visbreaking, the flowsheet includes the catalyst preparation and addition system upstream of the soaker vessel and additional desalting units on the final Aquaconversion liquid product to remove and recycle the Aquaconversion catalysts.

Claims: The key aspect of the Aquaconversion Process is the ability of a dual catalyst system to transfer hydrogen from water/steam to the heavy oil resulting in the ability to operate a visbreaker at higher severity with enhanced viscosity reduction.

The major claim is that the two catalysts, operating in concert, at 200 psig or lower pressure, and at the soaker temperature (825°F), provides hydrogenation of the vacuum residue preventing thermal degradation and resulting asphaltene and coke

formation. It is claimed that the hydrogen is obtained from the steam which is injected along with the catalyst. The chemical hydrogen consumption is equivalent to approximately 100 SCF/Bbl and is sufficient to result in a 4-7° API gravity increase of the product vacuum residue relative to the feedstock. This level of API gravity increase is insufficient to bring a typical Western Canadian heavy oil or bitumen to the pipeline specification of 19° API. With the higher residue conversions used in the Aquaconversion Process, the product viscosity is reduced below that from traditional visbreaking. Typically, the viscosity of the atmospheric residue is reduced by a factor of ten to over forty although the level of reduction appears to be feedstock related. For typical Athabasca bitumen, the viscosity of the whole bitumen at 7°C would need to be reduced from 12 MM (as produced from the froth treatment plant) to 350 cSt. This is not possible with the Aquaconversion Process.

The Intevep patents discuss the catalysts utilized in the process. The first catalyst is a Group VIII element and typically nickel, iron or cobalt is specified. According to the Aquaconversion publications, the function of the catalyst is to enhance the dissociation of water into hydrogen and oxygen free radicals. The hydrogen free radicals accelerate the thermal cracking rates of the paraffinic compounds and also stabilize the resulting thermal products by saturating olefinic free radicals. The second catalyst is an alkali element (sodium, calcium, magnesium, potassium) and typically sodium or potassium is specified. The function of the second catalyst is to minimize the condensation reactions which can result in coke formation, by promoting the addition of hydrogen to the aromatic free radicals. The best combinations of the two catalysts are stated to be Ni/K and Fe/Na. The catalysts can be added via a support or by direct addition to the feed steam via a soluble salt. The concentration of the total active catalyst metals (elements) in the feedstock are preferably above 1,000 Wppm (i.e., 0.1

W%). The net cost of the catalyst is unknown.

Product & Waste Issues: Based on the available publications, the high conversion Aquaconversion liquid product is reported to be stable as defined by the Shell P-Value test. In this test, Cetane anti-solvent is added to the liquid product to eventually result in asphaltene flocculation. The larger the quantity of Cetane which can be added without flocculation, the higher the P-Value and the more stable is the liquid sample. This stability test is a good indicator of both stability and compatibility.

The largest issue concerns the large concentration of catalyst in the Aquaconversion heavy product. At 50% conversion, the concentration will be twice that in the feed or over 0.2 W%. To address this, the process includes a second desalter (in addition to fresh feed unit). This unit operation and complex requirements may have contributed to the apparent difficulties in commercializing the process. Further study is required to completely assess the critical nature of this unit. Additionally, although not shown on the Aquaconversion flowsheet, the relatively large quantity of steam will eventually be condensed and may contain some of the catalytic salts. This water effluent will require treatment before reuse or disposal.

Scale-up: The scale-up from the Intevep 1 BPD pilot plant to an industrial size unit was accomplished via commercial tests conducted at PDVSA's Isla Curacao refinery. The commercial tests were deemed a success however the Aquaconversion Process performance was less than expected as a result of vessel and steam limitations. Since the commercial tests were performed in 1997 and the process is yet to be commercialized, there is a possibility that critical technical issues were uncovered and may not have been adequately addressed.

The current emphasis of development work (now suspended) on the Aquaconversion Process is related to the cost, usage rate and proper mixing of the two catalysts. This could indicate that catalyst cost, and handling of spent catalyst are the key shortcomings of the process.

Patents: Intevep has obtained two key U.S. patents covering the Aquaconversion Process. One was issued in 1997 and the second in 1999. The first patent primarily concerns the Aquaconversion catalyst formulation and the evaluation of different catalyst combinations. Good examples of visbreaking process results with and without the catalysts and with different catalyst combinations are provided in the patent. The second patent covers the process configuration and introduces the flowsheet as shown above, including the need for final product desalting. Many of the examples in the first patent are repeated in the second patent.

R&D Facilities: Intevep has operated a 1 BPD pilot unit in Venezuela which was used to initially develop the process. Pilot plant units at UOP may also be available for Aquaconversion R&D although no new technical papers or process updates have been reported in the past few years.

Current Status: In the past seven years the three firms (Intevep, Foster Wheeler and UOP) involved with the Aquaconversion Process have not been active in marketing the process. After many initial publications, press releases and conference presentations in the late 1990's, it appears that either the process has been partially abandoned or is under significant modification with additional R&D work and new developments in progress. It was discovered that according to a 2002 Foster Wheeler publication that "the process is still under development, with

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many crude types being investigated". This may indicate some level of development activity or simply a way to explain the lack of licensing success. It is interesting to note that the UOP website does not mention the Aquaconversion Process.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
Low Pressure Hydrogenation	Catalyst Make-Up Cost	Actual Catalyst Cost
Low Capital Investment	Cost to Remove/Recycle	Real Commercial Test
	Catalyst	Issues
Agreements with UOP and	Bitumen Product would	Catalyst Requirements for
Foster Wheeler	Require Diluent for Transport	Different Feedstocks
High (~50%) Conversion	Not Short Listed on Canadian	Issues with Water from
	Projects	Steam Injection
Deep Reduction in Liquid	No Commercial Plant +10	Current Plans for
Viscosity	Years after Process Announced	Commercialization
Good Pilot Plant Data		Current Development
		Status

The strongest strengths are the claimed low-pressure hydrogenation, moderate conversion operation and the alliances with UOP and Foster Wheeler. The demonstrated low pressure catalytic hydrogenation is a technical breakthrough although it is at a level which is insufficient for many applications and may not be an economical route. The largest weaknesses are the lack of a commercial reference after over ten years after the process announcement, and the inability to completely eliminate diluent for transporting Western Canadian feedstocks including Athabasca bitumen. The lack of a reference, including a retrofit of an existing visbreaker, is telling of issues with the technical features of the process (catalyst) and/or poor economics.

Best Applications: The Aquaconversion Process is best applied for retrofitting existing visbreakers and for new applications at refineries looking to reduce heavy fuel oil production. It may be applicable for partial upgrading for Venezuelan heavy crudes (Orinoco). This is due to the higher Venezuela ambient temperature and pipeline viscosity specifications higher than those in Western Canada. The process provides a 4-7°API gravity increase which is insufficient for producing transportable Athabasca upgraded crude. There is a remote possibility that it could be successfully applied to Cold Lake or Lloydminster heavy crudes which have higher API gravities and lower viscosities than Athabasca bitumen.

Summary: The Aquaconversion Process could be an effective route for a refinery to reduce fuel oil via additional conversion and flux requirements. Based on the Intevep patents and published patent claims, it does not appear that Western Canadian heavy oils and bitumen can be converted and hydrogenated sufficiently to produce a pipelineable product. This is a severe shortcoming for a Western Canadian application. The application of the Aquaconversion Process on Athabasca bitumen would reduce diluent requirements but would not be an economic choice. The process is not applicable to the partial upgrading route currently being investigated by many Western Canadian producers.

Catalytic Crude Upgrading (CCU) Process by UOP

Go To: Publications Patents

Process Name: Catalytic Crude Upgrading (CCU) Process

Company: UOP LLC, a Honeywell Company

U.S. Public Company

Website: http://www.uop.com

Process Overview & Objective: The CCU Process, announced in 2005, is an extension of the well-known FCC or RFCC process for cracking vacuum gas oil and heavier streams. The process objective is to process heavy crude and produce a transportable, higher API gravity, lower viscosity synthetic crude which will contain a significant quantity of vacuum residue. As such it is a partial upgrading process.

The CCU Process has two versions. In the first version, only a portion (~30%) of the heavy crude is sent to the RFCC Unit and the RFCC products are blended with the bypassed heavy crude to produce the specification SCO. Given that the heavy crude typically contains significant CCR, heavy metals and nitrogen, the RFCC coke yield and rate of catalyst make-up are very high. UOP does not discuss new or specific catalysts for the heavy oil CCU application. The flue gas from the regenerator will contain significant SO₂ and in most sites will require scrubbing or the use of limestone absorbent in a fluidized bed combustor. This is not discussed by UOP for this first process version. Version 1 is applicable to heavy oils with relatively low asphaltenes, CCR, and metals and has been initially applied (feasibility study/basic engineering) for a remote site in Columbia.

In the second version, which is more applicable to Athabasca bitumen feedstock, the entire heavy crude is first distilled with the atmospheric or vacuum residue treated in an SDA unit to remove all the feedstock asphaltenes. A portion of the DAO product is sent to a RFCC Unit as described for the first version. The DAO will have lower CCR, sulfur and metals than the RFCC feed to CCU Version 1

Process. The RFCC regenerator gas, containing CO, is burned along with the SDA asphaltenes in a fluidized-bed boiler which includes a limestone absorbent. The process will produce a large quantity of excess heat (steam) which can be used to produce electricity, requiring added investment. The bypassed DAO, RFCC product, and any straight distillates are blended together to comprise the final SCO. The Version 2 of the CCU Process can produce a transportable, specification SCO from Athabasca bitumen or Cold Lake type heavy oil. There is no secondary hydrotreating in either CCU Process version.

Claims: The FCC or RFCC process cracks the heavy oil in a short residence time riser in the presence of an active zeolite catalyst. The coke on the catalyst is burned off (regenerated) in a separate vessel and the catalyst recycled to the cracking riser. The FCC type process typically attains approximately 70% conversion of the 343°C⁺ in the feedstock and produces naphtha, diesel (LCO) and heavier (HCO or CO - Clarified Oil) products. The regenerator vessel partially combusts the coke with air to maintain low temperatures and insure adequate recycle catalyst activity. With high CCR feeds, the regenerator is designed with catalyst coolers to insure a unit heat balance. The resulting flue gas is completely burned in a CO boiler and if the unit is operated at elevated pressure (typical) the flue gas can be used to produce power in a letdown turbine. The FCC catalyst is poisoned by the metals and nitrogen in the feedstocks.

The Version 1 of the CCU Process is basically a RFCC with a portion of the feed bypassed and later combined with the RFCC product. There appears to be no novel invention, just an extension of existing technology. The process was developed in response to an inquiry from Meta Petroleum who was investigating processes to partially upgrade and enable transportation of their heavy Columbian crude from a remote area (no power and possibly no natural gas availability) to a

coastal refinery. Due to the nitrogen and metals in a typical heavy oil, the rate of catalyst make-up is very high, nearly 1 Lb/Bbl of feed. The key challenges for the Version 1 process are the development of methods or new catalysts for reducing the catalyst make-up rate.

A comparison of the properties of the Meta Petroleum and Athabasca Bitumen crudes is shown in the table below. Athabasca bitumen contains significantly

higher metals and sulfur and is significantly more viscous. Although not shown in the table, the Athabasca bitumen asphaltene content is also much higher. It is possible that UOP

	Columbian	Athabasca
Gravity, °API	12.8	8-9
Sulfur, W%	1.3	4.9
CCR, W%	12.9	13.5
Nickel, Wppm	42	75
Vanadium, Wppm	152	250
Viscosity @50°C, cSt	930	~10,000

realized that the Version 1 CCU Process could not feasibly handle this heavier feed and developed the second process version as described in their key patent application.

The Version 2 CCU Process adds a solvent deasphalter of the whole crude stream ahead of the RFCC Unit. A portion of the DAO product is processed in the RFCC and a fluidized-bed combustor to burn the regenerator gas and asphaltenes. This again is basically a combination of well-known processes and presents no novel chemistry or technical breakthroughs. The Athabasca DAO will have lower metals and CCR than the Columbian crude and will be easier to process. DAO is commercially processed in RFCC Units but not comprising 100% of the RFCC feed. The removal of the asphaltenes, comprising 15-20% of the feed will result in a large reduction in the net SCO yield. Additionally, there will be a large quantity of excess energy which UOP claims should satisfy both the Upgrader and upstream SAGD energy requirements.

Overall, the process is technically sound but when applied to Athabasca bitumen

will have low liquid yield and high investment and operating costs. If all of the

bitumen or DAO is processed in the RFCC step, the process could be considered a

near-full upgrading process. This may be more appropriate given the CCU

complexity and high required investment.

Product & Waste Issues: There are no stability or waste issues related to the

CCU liquid product. The only waste issue is the venting of the final regenerator

flue gas which for most sites will require scrubbing or burning in a fluidized-bed

combustor with absorbent.

Scale-up: The CCU Process performance and yield data is presumably based on

commercial data and scale-up is not an issue for any of the process steps.

Patents: In February 2007, UOP published an instructive patent application for

both versions of the process. Since the CCU Process is really a combination of

well-known processes on a portion of the heavy oil feed, the patent application

may not be granted. The patent application provides good examples but does not

discuss the catalyst usage rate or amount of excess energy. Three additional UOP

patents are listed in *Attachment 2*; these discuss a catalyst formulation (portion is

zeolite) which can be applied to heavy crude processing in the FCC. It is

uncertain if the three additional UOP patents are applicable to the CCU Process.

R&D Facilities: UOP has sufficient R&D facilities to optimize the process and to

perform feedstock evaluations. Complete demonstration of the individual process

steps is not necessary.

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Current Status: It appears that the CCU Process was developed in 2005 in response to the inquiry from Meta Petroleum. UOP has not aggressively marketed the process. The major current activities are:

- Collaboration with Albemarle and Petrobras In October 2008, UOP announced an agreement with Albemarle (catalyst manufacturer) and Petrobras to demonstrate and commercialize the CCU Technology. Albemarle is developing an improved FCC catalyst specifically for the process. Petrobras (owner of Meta Petroleum) has demonstrated the CCU Process in their Brazilian pilot plant.
- 2. Meta Petroleum Project UOP completed the basic engineering sometime in mid-2006. There are two parallel CCU Units planned for the 100,000 BPSD complex. A relatively low investment of \$700 for the Upgrader and product pipeline was quoted in a news article. There have been no updates on the project since mid-2006.
- 3. Other Projects UOP reports that they are working two additional CCU Projects for "stranded" crude oil reserves.
- 4. <u>Patent Application/NPRA Paper</u> These two sources are the only available information on the CCU Process.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the CCU Process, specifically Version 2 which is applicable for bitumen feedstock, is shown on the next page.

Strengths	Weaknesses	<u>Unknowns</u>
UOP Licensed	High Catalyst Make-Up Cost	Will UOP Actively Market
Proven SDA & RFCC Technologies (Fully Developed)	Low Liquid Yield	Comparison with EB or Coking -Yields, Economics
Meta Petroleum Project	High Investment Cost	Patentability of Process Steps
Produces Pipelineable SCO	No Process Novelty	Al and Si Fines in SCO
No Residual Product	Net Energy Exporter	Current Commercialization Status
No Hydrogen Required	Multi-Step Complex Process	
Energy Self Sufficient		
Catalyst Collaboration with Albemarle		

The greatest strengths are that the process is licensed by UOP and produces an acceptable partial upgraded SCO without hydrogen addition. The large quantity of excess energy would fit well with a SAGD application. The greatest weaknesses are the high catalyst make-up rate and cost, estimated high investment and low liquid yield. Considering that the process produces a sour partially upgraded SCO, the overall process is fairly complicated requiring significant equipment and process steps.

Best Applications: The CCU Version 1 Process is best applied for niche applications such as the Meta Petroleum Project in Columbia. The Columbian heavy crude is less viscous and contains less contaminants than typical Western Canadian heavy oils and bitumen. Additionally, environmental regulations for this niche application in Columbia may be less stringent allowing for direct venting of the flue gas.

The Version 2 CCU Process is more applicable to Western Canadian heavy oils and bitumens which are more sour and contain higher levels of metals, asphaltenes

and CCR. The process can attain typical pipeline specifications and meet environmental regulations with the use of a fluidized-bed combustor. The Version 2 process may be most applicable to full upgrading given the process complexity and required investment. This would simply entail the elimination of any crude or DAO bypass around the RFCC step.

Summary: The partial upgrading CCU Process can be applied to Western Canadian heavy oils and bitumen and produce a specification, transportable sour SCO. The economics of the process, given the estimated high initial investment, low liquid yield and high catalyst cost, are in serious question.

Further investigation the CCU Process for partial upgrading would require estimation of the investment, liquid yield, product quality and profitability and comparison with a well-defined partial upgrading process such the Ivanhoe HTL Process or using ebullated-bed hydrocracking.

CPJ Process

by Wesco Energy Corp.

Go To: Publications Patents

Process Name: CPJ Process

Company: Wesco Energy Corp., Conroe, Texas

U.S. Private Company

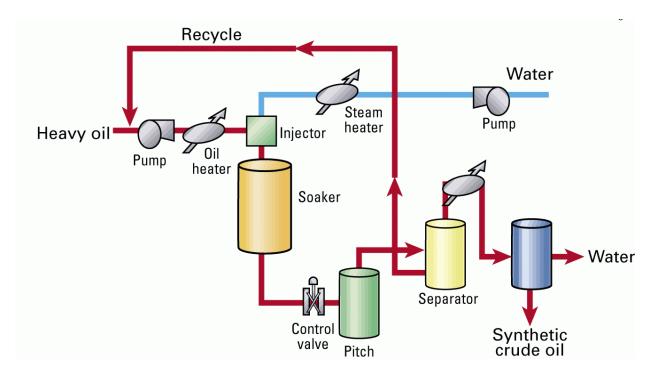
Website: http://www.wescoenergy.net (not active Nov /2010)

Process Overview & Objective: The CPJ Process is a thermal cracking technology which produces a sour SCO and an unconverted heavy oil (pitch) product which can be oxidized to produce steam and/or power. The CPJ Process is a partial upgrading technology since a small portion of the vacuum residue in the heavy crude feedstock will remain in the liquid product. Wesco is targeting a field upgrading application for the CPJ Process. The process was invented by Dr. Pierre Jorgensen in the early 1990's. The process is akin to visbreaking in that the feedstock is mildly thermally cracked and no significant coke product is claimed.

The process was originally developed in France by Dr. Pierre Jorgensen and rights acquired in the 1990's by a joint venture of Texas T Resources (Calgary) and Synergy Technologies (Texas). In 2001, Synergy obtained 100 percent ownership in the technology and constructed and operated a pilot plant in Calgary (2000) which was eventually moved to Conroe, Texas. In March 2003, the CPJ and other Synergy processes were acquired by private concerns that formed Wesco Energy Corporation.

A simplistic process flow diagram for the CPJ Process is shown on the following page. The feedstock can be full range crude in the case of heavy oils/bitumen or can be atmospheric or vacuum cuts in the case of lighter crudes. The feedstock is preheated to approximately 840°F and pressurized to 250–450 psi. It is then combined with superheated steam (1,100°F) and sent though an injection nozzle and into an empty soaker reactor. The feed oil to steam ratio is on the order of 1/1. The feed may also include recycled unconverted residue and vacuum gas oil

(VGO). The soaker reactor operates at 860-880°F with a residence time of less than 1 minute. The CPJ reactor temperature is significantly lower than the temperatures used in a delayed coker. Conversion reactions occur as a result of the nozzle/reactor temperature and the kinetic energy released in the specially designed nozzle.



According to Wesco, the reactions are significantly less severe than coking and preferentially crack the heavy oil residue into relatively large molecules rather than into smaller molecules which would include light gases and would also lead to coke formation. Additionally, the presence of the steam and the moderate pressure operation allows for some capping of the hydrogen deficient conversion products. This aids in maintaining a stable conversion liquid product. The products from the reactor are depressurized and then separated into water, pitch (unconverted residue) and distillates which can eventually form a SCO product. In a commercial plant, the recovered water is treated and recycled for steam injection.

The distillate products from the CPJ Process will contain significant water and standard distillation for product recovery is not feasible. Extractive distillation or other techniques are required to break the oil/water emulsion and to produce acceptable liquid products. This adds complexity to the process and may result in possible scale-up issues. Undesirable light gas yields are low and according to Wesco, are almost insignificant.

Wesco touts the CPJ Process as a diesel process since there is a high selectivity to diesel range material. This is a direct result of the recycle of VGO back to the CPJ reactor system and its conversion to diesel range material and lighter. It is not clear if a once through (i.e., no recycle) operating mode would produce stable product meeting typical pipeline specifications product. Recycle of any unconverted product in the CPJ Process will increase the net SCO API gravity and will decrease viscosity but will reduce the maximum feedstock throughput (BPD) for a given size CPJ Unit.

The pitch product has low utility and is typically burned to produced steam and/or power. The high sulfur content dictates that a fluidized-bed type combustor with a limestone absorbent be specified. The cost of the pitch combustor is a significant portion of the overall CPJ Process investment cost. Operating conditions in the CPJ Process could be adjusted to produce sufficient steam for a SAGD operation at the expense of SCO yield. However, it may be economically advantageous to maximize CPJ SCO yield (low pitch yield) and utilize supplemental natural gas or raw bitumen/heavy oil for producing the required process and SAGD steam.

Claims: The critical aspects of the CPJ Process are related to the benefits from thermally cracking at low temperature and optimized pressure, residence time, and steam partial pressure. These benefits minimize or eliminate over cracking of the

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heavy oil which can lead to high light gas yields and coke production. The CPJ patent claims that hydrogen originating from steam is used to cap free radicals resulting from the cleavage of heavy oil bonds. This means that the CPJ Process

consumes hydrogen and that the hydrogen originates from the water/steam fed to

the process. This is an important claim and can be verified though a precise water

and hydrogen balance around an experimental unit.

Based on the data published by Wesco, these claims appear to be substantiated

although the hydrogen consumption via water/steam is not verifiable. There is a

small net coke make, very low gas yields and the product appears to have fairly

high quality and long-term stability. The small coke production requires that the

soaker reactor and other components be periodically cleaned resulting in unit

shutdowns. The frequency of this turnaround is unknown and may be a significant

operating cost issue.

Product & Waste Issues: The CPJ Process produces a heavy hydrogen deficient

liquid product, spent lime (gypsum) from the fluidized-bed boiler and a

combustion flue gas. Because of the use of the lime, the flue gas should be an

acceptable effluent. The gypsum product may present a disposal issue depending

on the plant location.

Directionally, the CPJ liquid product will be more stable and of better quality than

that produced from a delayed coker. This a result of the lower temperature

operation and the shorter residence time of the conversion products in the reactor.

Of the thermal cracking processes investigated, the CPJ Process produces liquids

which have one of the highest probabilities of being stable. In addition to stability

testing, the compatibility of the liquids with lighter oils and typical refinery

feedstocks should also be tested.

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Scale-up: The CPJ Upgrading Process has not been commercialized. Small-scale laboratory experiments were conducted in France to initially develop and optimize the process. A one BPD pilot plant was constructed in Calgary and moved to Conroe Texas where it is currently located. The unit is the "work horse" for evaluating feedstocks and developing client yield estimates. Typical pilot plant tests are short in duration (<24 hours) and thus will not provide equilibrium or steady state performance when recycle is utilized. Additionally, for heavy feedstocks containing significant contaminant metals, there may be a long-term build-up of insoluble metal compounds (e.g. V₂O₅ or vanadium pentoxide) which

A 50 BPD CPJ demonstration facility was constructed in Texas to alleviate concerns relative to the nozzle and soaker design/operation and scale-up. The larger unit operated successfully for approximately 10 months and was shut down. Similar to the pilot plant, this unit also operated for short run lengths with a maximum duration of a few days.

would not be observed in the pilot unit.

Given the successful scale-up from 1 top 50 BPD, the largest remaining scale-up issue is long term continuous operation and observance of erosion, solids build-up and other unforeseen issues.

Patents: One issued U.S. patent concerning the CPJ Process was found. Other patent or patent applications may exist but may not have been assigned to Jorgensen, Synergy, or Wesco. Dr. Jorgensen (assignee: Wesco) was granted the patent in January 2006. The Jorgensen patent is extremely technical and lengthy but is comprehensive in terms of a theoretical explanation of CPJ Process. Much of the discussion above is based on this patent. The patent also contains process yields and product qualities and appears to give-away much of the technology. It

is surprising that there are no patents or applications relating to the CPJ reactor nozzle design.

R&D Facilities: Small-scale experiments were conducted in France (Jorgensen) to initially develop and optimize the original process. An approximate 1 BPD pilot unit was constructed in Calgary and moved to the Wesco offices in Conroe Texas where it is still available for testing. This unit operates for short run lengths (< 24 hours). This unit is utilized for feedstock and yield estimates. Over 300 runs on over 30 feedstocks have been conducted in the unit.

A larger 50 BPD unit was built and operated in Texas in 2003/2004 but is shut down and no longer available. An approximate 2,000 BPD demonstration plant is planned, pending funding.

Current Status: The CPJ Process was acquired by Wesco in March 2003. Since acquiring the technology, the company's emphasis has been on commercializing the technology, although there has not been a high level of publications and press releases. The following activities have been observed from the company website and available publications:

- 1. <u>Pilot Plant</u> Construction and operation of 50 BPD pilot plant in Texas which is no longer available. The unit was constructed to verify scale-up as part of a possible joint venture with a prospective CPJ client.
- 2. <u>Technical Evaluations</u> Third party evaluations were conducted by Strategic Management Inc. (2004) and Burns & McDonnell (2005). According to Wesco, these evaluations were positive. The latter study resulted in the development of a detailed design package and a capital cost estimate for a 5,000 BPD unit. The capital estimate was reported to be in agreement with an independent estimate by Purvin&Gertz.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the CPJ Process are shown below.

Strengths	Weaknesses	<u>Unknowns</u>
Good Technical Patent	No Long-Term Testing –	Feasibility of Processing
Discussion	Erosion, Solids Build-up Issues	Very Heavy Crude
Sound Technical Approach	Inability to Commercialize	Degree of Recycle to Meet
	after 15 Years	SCO Pipeline Specifications
Strong Technical Staff	Small, Newly Founded	Scale-up - Solids Dep. &
	Organization	Extractive Distillation
No Catalyst and H ₂ Required,	Product Stability/Compatibility	Economics for SCO
Small Net Coke Product	Concerns	Production
Can Fit with SAGD Projects	Cost of Fluidized-Bed	Reasons for Failed
	Combustor	Commercialization Projects
Low Light Gas Yields	Large Process Steam	
	Requirement	

The greatest strengths are the sound technical approach, resulting in enhanced liquid yields and qualities and a high potential for stability, and low light gas yields. The greatest weaknesses are the lack of long-term testing, reasons as to why prior commercialization efforts failed, and the potential for unstable/incompatible liquid products.

As with similar thermal cracking type partial upgrading processes, the final process profitability when using the recycle mode of operation and producing a large quantity of energy are also questionable.

Best Applications: According to the Wesco publications, the CPJ Process can produce a +20°API SCO from Western Canadian heavy oils including Athabasca bitumen. The process produces a low value pitch product which can be burned to produce significant steam. The process is most applicable to SAGD operations. A field application at or near the SAGD site is also preferred since the process does

not require hydrogen and catalyst and could possibly generate power.

Summary: Based on the technical information available, the CPJ Process has potential for eventual commercialization. This is based on the unique reactor concept, pilot plant and 50 BPD demonstration plant operations, and published data supporting that the process can produce a specification partially upgraded SCO from Western Canadian heavy oils. The failures at commercializing a few years ago are of concern. The market value and stability and compatibility of the thermally cracked SCO are questionable although Wesco's approach and published data support the production of a stable product. Further evaluation of the process would include obtaining laboratory and pilot plant data and estimating project profitability.

EADIEMAC Process

by Eadie Oil Inc.

Go To: Publications **Patents EADIEMAC Process**

Process Name:

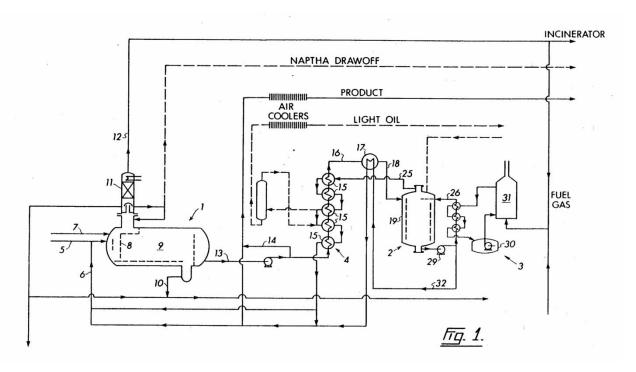
Company: Eadie Oil Inc., Edmonton, Alberta

Private Canadian

Website: http://www.eadie.com

Process Overview & Objective: The EADIEMAC Process is a combined froth treatment / visbreaking process specifically developed for Athabasca bitumen. The process is fairly complex and produces a visbroken product which does not meet typical pipeline specifications (19°API and 350 cSt at 7°C). Besides the upstream froth treatment, which is deemphasized in the EADIEMAC patent and their website, the other novel feature is the indirect heating of the oil using a eutectic salt mixture which is heated in a fired heater. According to Eadie Oil, this results in milder visbreaking conditions and reduced coking.

A process flow diagram for the EADIEMAC Process, taken from the issued patent, is shown below. The diagram is unnecessarily complex and includes numerous secondary equipment and optional streams. The process operates at



approximately 50 psig. The heavy oil feed, containing water and solids is stream 5 and enters the coalescing vessel 1. The feed is mixed with relatively hot heavy product 6. Water/solids are removed from the settling portion of the coalescing vessel via stream 10. The feed/product oil mixture (stream 13) is exchanged with hot vapors and liquids and enters the "flash separator", vessel 2 in the diagram. The inner portion of this vessel is the soaker where the visbreaking reactions occur. The soaker vessel has an internal ring which separates the feed heating/soaker cooler sections of the soaker vessel. In the outer annulus, the feed oil is heated via transfer from the inner soaking section. A mixture of visbroken residuum and heavy oil at 730-800°F is fed to top of the soak chamber. There is heat transfer through the ring from the soak liquid to the annulus liquid to assist in maintaining the mild temperature in the soak chamber. The two streams mix in the base of the vessel whereby the visbreaking reaction is quenched. Part of the product is recycled and indirectly heated to provide the feed to the soak chamber. The recycle liquid (steam 26) is heated via transfer with the hot eutectic salt mixture. The salt solution is heated via fired heater 31.

Claims: The EADIEMAC Process is a thermal visbreaking process which does not use catalyst or require hydrogen. The major process claim is that the indirect heating of the oil using a eutectic salt mixture results in milder visbreaking conditions and reduced coking. There is no supporting data to confirm this claim.

Rather than touting a new and improved visbreaking process, the Eadie Oil website concentrates on the merits of partial upgrading and the reduction and possible elimination of diluent to transport a heavy crude oil. Economics are presented which can be applied to any partial upgrading route. The scale-up of the process, the actual commercial investment cost, and the marginally stability of the visbroken product are major concerns.

Product & Waste Issues: To my knowledge, visbreaking has not commercially applied to Athabasca bitumen. The probable reasons include the inability to meet pipeline specifications (i.e., diluent required to transport) and the possible instability of the product. Athabasca bitumen has high CCR and asphaltene contents; the limit of a visbreaker conversion, as measured by product stability, is quickly reached. An additional issue with EADIEMAC Process, particularly with a field application, is the production of a sour fuel gas which cannot be burned and vented to the atmosphere.

Scale-up: The EADIEMAC Process has been piloted in a 1½ BPD unit and the need for a 500-1,000 BPD demonstration plant is stated in their website. Scale-up of the process reactors, the coalescing and flash vessel (soaker) may be difficult. Eadie Oil discusses relatively small modular units which can be shipped to a site. This may alleviate some scale-up issues.

Patents: There is a U.S. patent assigned to Eadie Technology with inventors W. Eadie and W. MacWilliams. The patent was filed in 1988 and issued in 1992. The patent is fairly well written (process features explained) and contains batch and continuous process data on three heavy oils, not including Athabasca bitumen. The data shown illustrate typical visbreaking results with an approximately 4°API increase and significant viscosity reduction. The product viscosities shown in the patent do not meet the current Canadian pipeline specification values.

R&D Facilities: Eadie Oil has operated a 1½ BPD pilot plant located near Edmonton. There are no details as to the extent to which the commercial process was piloted, the number of tests, test duration, etc. The size of the pilot facility appears to be fairly large; however it may have been batch and operated for

relatively short test durations. According to their website, Eadie Oil is in the process of looking for a site (and financing) for a 500-1,000 BPD demonstration plant.

Current Status: The owners of Eadie Oil (Bill Eadie and Bill MacWilliams) do not appear to be highly active in marketing their process. There are no publications, news coverage or presentations at technical seminars. The website is the only source of information. The PowerPoint presentation on the Eadie Oil website is dated November 2008 and may indicate some renewed interest in finding assistance in fully developing the process.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the EADIEMAC Process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
Combined Froth Treatment and Visbreaking	Does not Meet Pipeline Specifications	Economics Relative to Existing Visbreaking Processes
Indirect Heating of Residue	Process Complexity	Process Scale-up
Process Flexibility	Product will be Unstable or at Limit of Stability	Stability of Product and Typical Diluent Blend
	No Demonstration Plant	Process Maintenance Issues
	Newcomer to Upgrading	

The greatest strengths are the possibility of combining froth treatment and initial upgrading and the indirect heating of the residue. The former strength is not currently touted by Eadie Oil and may indicate some issues with the coalescing step. The greatest weaknesses are the inability of the process to achieve pipeline specifications, the process complexity and the creation of a SCO product at the

limit of stability. A large unknown is how the EADIEMAC process economics, primarily investment, compares with the well-demonstrated commercial visbreaking processes.

Best Applications: As with any visbreaking process, the best application is for reduction of heavy fuel oil product and the production of increased distillates and VGO. If the EADIEMAC process claims are correct, refiners in the U.S and Western Europe should be interested in the further development of the process. Application for partial upgrading in Western Canada is doubtful. Given the modular design suggested by Eadie Oil, application for SAGD may be their current target.

Summary: The EADIEMAC Process is not fully developed and may or may not have advantages over existing visbreaking processes. The process patent was issued in 1992 and it does not appear that the technology has significantly advanced. The process is not applicable to the partial upgrading route currently being investigated by many heavy oil and bitumen producers. Only if the demonstration plant is eventually financed and constructed would the process warrant further investigation.

Heavy to Light Oil (HTL) Process by Ivanhoe Energy Inc.

Process Name: Heavy to Light Oil (HTL) Process Go To: Publications Patents

Company: Ivanhoe Energy Inc., Vancouver, British Columbia

U.S. and Canadian Public Company

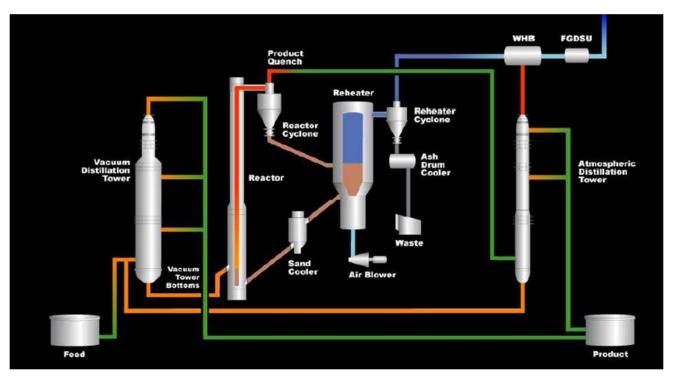
Website: http://www.ivanhoe-energy.com

Process Overview & Objective: The HTL Process is a developing, near-commercial, thermal pyrolysis / partial coking / coke combustion technology which produces a relatively low yield of heavy product (SCO) and a considerable amount of excess energy usually in the form of steam. HTL is a partial upgrading process since a portion of the vacuum residue in the heavy crude will remain in the HTL SCO product. The process was invented by the Ensyn Group in the 1980's for the conversion of wood and other biomass fuels. Six, relatively small biomass commercial plants have been constructed and operated. These biomass facilities produce a "bio-oil" or "bio-fuel" and carbon from wood and other organic wastes.

Beginning in the late 1990's, Ensyn initiated an additional development program to extend the application of the process to the partial conversion of heavy oil and bitumen. In 2005, the rights of the process as applied to petroleum feedstocks were sold to Ivanhoe Energy. The HTL Process was originally called RTP (Rapid Thermal Processing).

HTL Process performance is accomplished by conversion of a large portion of the vacuum residue as in a coking process with accompanying energy export resulting from the combustion of the coke. Recycle of the unconverted atmospheric or vacuum residue is specified to increase the overall level of vacuum residue conversion and the API gravity of the net HTL product. The recycle will also decrease the viscosity of the net HTL liquid product.

A process flow diagram for the HTL Process is shown below. The process operates at low pressure and is similar in concept to a FCC Unit. The process is fairly complex and incorporates critical design features which are paramount to attaining the liquid yield and quality required for the process to be competitive for heavy oil processing. In the HTL Reactor system, the feed oil is initially fractionated to produce vacuum residue and distillate products which are routed to product blending. The vacuum residue is mixed with a hot inert carrier (from the sand cooler). The oil is very quickly raised to high temperature where pyrolysis and thermal cracking occurs. The coked sand and conversion vapors are quickly transported in the HTL riser-type reactor.



The residence time in the reactor and cyclone separators is very short and the heavy liquid product is quickly quenched using distillate HTL product. The rapid heating and short residence time are key aspects of the technology and insure that the reactions are stopped prior to full progression to unstable thermally cracked or coking-type products. The hot carrier (sand), which is captured in the cyclones,

will contain coke and other heavy material which are deposited on its surface.

This carrier is "regenerated" in the sand reheater to burn-off the coke and to provide a reheated carrier for the HTL Reactor. Complete combustion with air has been specified. The non-condensable light hydrocarbon gases which are produced in the HTL Process can also be burned in the regenerator. The flue gas from the regenerator must be treated (limestone absorbent) before venting to the atmosphere. For a heavy oil or bitumen feedstock with a high CCR content, the combustion results in a very large quantity of excess heat in the form of steam. The liquid product obtained from the product distillation column will contain naphtha, diesel, VGO and unconverted atmospheric residue. These are blended together along with the straight run distillates to form the final SCO product. The atmospheric bottoms from the HTL product distillation tower can also be recycled to the HTL feed vacuum fractionator to increase the level of residue conversion.

For very heavy feedstocks or to provide deep viscosity reduction and API gravity improvement, it is necessary to recycle the heavy HTL liquid product (atmospheric or vacuum residue) back to the reactor for additional vacuum residue conversion. This mode of operation ("high quality mode") will result in high quality SCO but with a lower net liquid yield, more excess energy and a smaller feedstock capacity in a specific size HTL Unit. A bottomless operation (< 5% vacuum residue in SCO) with near complete extinction of the feedstock vacuum residue is also possible at the expense of liquid yield and more export energy. Operation of the HTL Process without recycle is termed the "high yield mode" and will have relatively poor SCO product quality.

Claims: The critical aspects of the HTL Process chemistry are rapid feedstock heat-up rate via mixing with the hot carrier and a short reaction residence time of

less than a few seconds with minimal back-mixing (i.e., plug flow).

The above aspects result in fast pyrolysis which stops the thermal chemical reactions before the intermediates can degrade to non-reactive products such as coke. A significant claim of the HTL Process is reduced coke yield relative to traditional delayed or fluid coking processes. Key design aspects are the initial mixing of the hot carrier and feedstock and the transport type reactor. The latter feature must include a relatively high velocity with minimal back mixing to avoid any particle or vapor residence time distribution.

In September 2009, Ivanhoe announced a HTL Process breakthrough wherein the required quantity of recycled residue to attain a high level of product quality is reduced by 80 percent. This was demonstrated in the newly commissioned HTL pilot plant and was attributed to improved short residence time cracking. Ivanhoe reported that the breakthrough results from higher once-through (no recycle) conversion rates and is reported to have minimal effect on the SCO volumetric yield. A possible explanation for the higher conversion rate of straight run residue is higher local reaction temperature or increased residence time. This would be evidenced by higher coke and light gas yields and less weight liquid yield. The higher conversion of straight run and conversion VGO would also result in a lighter product yield slate (i.e., more naphtha and diesel in the SCO). This would be evidenced by a lower weight SCO liquid yield but an unchanged or a slightly lower volumetric liquid yield.

The quality of the HTL diesel and VGO products is similar to delayed coker liquids and will eventually require significant hydrotreating. This will result in a price debit for the HTL SCO relative to a fully upgraded material. The stability of the product is of concern. As a result of the relatively poor HTL distillate quality,

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the vacuum residue content of the SCO must be reduced to less than

approximately 10% to meet Canadian gravity and viscosity specifications. This is

contrasted to a hydrogen addition partial upgrading process with higher quality

distillates where the specification SCO contains 25-30 V% vacuum residue.

The HTL Process does not utilize a catalyst or require hydrogen. The inert carrier

used to heat the feedstock and provide a surface for coke deposition is typically

sand. Long-term tests are required to adequately assess the equilibrium

fluidization characteristics of the sand as it builds up coke and metals and goes

through multiple thermal cycles.

Ivanhoe adds calcium hydroxide (lime) with the crude feedstock. The lime serves

two functions. It neutralizes the acids in the crude distillates (reduces TAN value)

and provides a sorbent for sulfur removal in the coke combustion step (reheater).

Product & Waste Issues: The HTL Process produces a heavy hydrogen deficient

liquid product, spent lime (gypsum) and a combustion flue gas. Because of the

use of the lime, the flue gas should be an acceptable effluent. The large quantity

of gypsum product may present a disposal issue depending on the plant location.

The HTL liquid product should be similar to that produced from a delayed coker

although Ivanhoe claims that it is stable as evidenced by their stability studies. The

stability and compatibility of the HTL products are of concern, particularly at

higher conversion.

Scale-up: The HTL Process operating on a petroleum feedstock has not been

commercialized. The process configuration has been applied to biomass

conversion (wood, lignin) and there are several small commercial size units. The

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size of these units is equivalent to 300–1,000 BPSD of a heavy oil feedstock. For an Athabasca vacuum residue feedstock, the equivalent throughput is approximately 300 BPSD of vacuum residue and even less for the recycle operating mode.

The scale-up from the 5-20 BPD Ensyn pilot plant to the demonstration facility (250-1,000 BPD) was accomplished in 2005. The HTL demonstration plant started-up in December 2004. Additional scale-up from the demonstration facility to a commercial size HTL module (10,000 BPSD) should not be difficult.

Patents: The HTL Process has an adequate patent portfolio. Two U.S. patents were issued to Ivanhoe in August 2009 describing the inclusion of a calcium additive with the heavy oil feedstock. A September 2007 U.S. patent specifically addressing the HTL Process as applied to petroleum feedstocks is the first patent assigned to Ivanhoe. It is well written and instructive as to the process details. A U.S. patent application was filed in September 2008 and covers bottomless SCO production and integration with a heavy oil production facility. Several older U.S. and Canadian patents originally assigned to Ensyn were also found. These are very instructive as to the design of the reactor and circulating carrier system. The older patents are more specific to the treatment of biomass and wood.

R&D Facilities: Ensyn operated a 5-20 BPD pilot facility in their R&D center in Ottawa. This was utilized for both biomass and heavy oil studies with over 90 tests conducted for heavy oil feedstocks. Additionally, a 250-1,000 BPD (depending on feedstock residue content) HTL demonstration plant was started-up in December 2004. The demonstration plant is located near Bakersfield, CA and is now owned by Ivanhoe Energy. The facility has performed initial successful testing as evidenced by an \$800,000 (Can) payment to Ensyn from ConocoPhillips

in return for non-exclusive rights to the HTL Technology in Canada for capacities up to 25,000 BPSD.

The demonstration facility did not have sufficient feed and product storage facilities and thus run lengths were limited to just a couple of days. Additionally, the demonstration unit had only a single atmospheric fractionation still (no vacuum still), limiting the possible feed and recycle liquid cutpoints. It will be completely decommissioned by mid-2010.

In March 2009, Ivanhoe successfully commissioned a new smaller pilot plant (Feed Test Facility or FTF) at the Southwest Research Institute in San Antonio, TX. The plant processes 5-15 BPD and should be capable of longer term tests. Importantly, the FTF can operate continuously with vacuum residue feedstock to the reactor and with recycle of unconverted residue. A test on Athabasca bitumen was completed in May 2009. The test was deemed successful; however detailed results and the test duration have not been published.

Current Status: Listed below are some of the important items concerning the HTL Process.

- 1. Contract with Petroecuador In October 2008, Ivanhoe signed a contract with the state oil company of Ecuador (Petroecuador) to explore and to develop the Pungarayacu heavy oil field utilizing the HTL technology. The payment to Ivanhoe will be indexed and adjusted \$37/Bbl of oil produced. The reserves are estimated at 6.4 B Bbl of oil in-place with an API gravity of 13.5 to 14.8°. In May 2009, approvals were received from Ecuador to initiate permitting and the initial phase of the project and the first well was drilled in December 2009.
- 2. Tamarack Project In May 2008, Ivanhoe signed an agreement with

Talisman Energy Canada to acquire Talisman's interests in three Athabasca leases for C\$105 MM. At that time, Ivanhoe stated that this will be the site for the first commercial HTL Unit. The Tamarack reserves were estimated (2009) at 440 MM Bbl of oil in-place, sufficient to support a 50,000 BPD HTL Upgrader. The first phase is a 20,000 BPSD HTL phase (cost = \$1.25 B) with basic engineering completed in July 2009 and an updated cost estimate slated for mid-2010. As of March 2010, the initial drilling program was one-half complete and a regulatory application will be submitted in mid-2010.

- 3. Demo Plant The 250-1,000 BPD demonstration plant located in Bakersfield, CA was initially operated in 2005. The facility performed successful initial testing as evidenced by a payment to Ensyn from ConocoPhillips in return for non-exclusive rights to the HTL Technology in Canada. The plant performance was evaluated by Purvin & Gertz to certify the ConocoPhillips payment. The demo plant went through two periods of significant modifications in the mid-2005 to mid-2006 time period. Less than twenty, 24-48 hour tests have been completed. It appears that all but one test (on Athabasca bitumen) were conducted on California heavy oils.
- 4. MOU with Ecopetrol In December 2004, Ivanhoe executed a MOU with Ecopetrol to study the upgrading (transportation from remote field) of Castilla and Chichimene crudes including demonstration plant tests. The tests were never conducted. The current status is unknown.
- 5. <u>Iraq</u> In October 2004, Ivanhoe signed a MOI with Iraq's Ministry of Oil to study the application of the HTL Process for Iraqi heavy oil. In April 2007, Ivanhoe and INPEX Corp. signed an agreement to jointly pursue the Iraqi opportunity. Ivanhoe maintains a majority interest in the project and obtained a cash payment from INPEX. INPEX is a major Japanese oil and gas development company.
- 6. <u>Aera Energy</u> A December 2004 press release announced a non-binding agreement between Ensyn and Aera Energy (Shell and

Exxon/Mobil joint venture) to build a 10,000 BPSD HTL Plant in California. This project is still being pursued by Ivanhoe.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the HTL Process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
Good Patents / Applications	Process Complexity	Market Valuation of HTL SCO
Agreement with Petroecuador	No Long-Term Test in	Real Economics for SCO
	Demo Unit	Production
Demo Plant Size	No Petroleum Commercial	Degree of Recycle to Meet
	Reference	SCO Pipeline Specifications
Strong Technical Staff	Flue Gas Treatment	Applicability to Athabasca
Subing Teemment Starr	True Gus Treutment	Bitumen
No Catalyst and H ₂ Required,	Poor Quality Products /	
No Coke Product	Product Stability Concerns	
Tamarack Project		
Fits with SAGD Projects		

The greatest strengths are the recent agreement with Petroecuador, the Tamarack Project in Alberta, technical knowledge of key employees, and that Ivanhoe is focused and highly committed to near-term commercialization. The successful operation of the new smaller test facility with a long-term test will be a key item for HTL Process commercialization. The greatest weaknesses are the process complexity, the poor quality product, and the marginal application for partial upgrading of Athabasca bitumen.

The final process profitability when using the recycle mode of operation and producing a high level of excess energy are also questionable.

Best Applications: The HTL Process is a partial upgrading technology which produces significant excess energy. Given the large quantity of excess energy

from the burning of coke, the HTL Process is most applicable to SAGD projects. The Ivanhoe target market is possibly these SAGD projects along with other heavy oil deposits in the U.S. and China and remote locations (e.g. Columbia and Ecuador). HTL Process feedstocks with vacuum residue and CCR contents lower than Athabasca Bitumen and locations where pipeline specifications are less severe, may show better process yields and economics. This would include California and Venezuelan heavy crudes as well as "stranded crudes" which are located far from pipelines, natural gas wells and electric power grids.

Summary: The HTL Process has potential for producing a specification partially upgraded SCO from heavy oils from California and other regions. HTL has a marginal application to Athabasca bitumen and other Western Canadian heavy oils which require the high quality (recycle) mode of HTL operation. The stability and compatibility of a hydrogen-deficient SCO is of concern. The process fits very well with SAGD projects due to the excess energy produced but only if the economics and stability concerns are resolved. Ivanhoe appears to be committed to fully developing and commercializing the process.

H-Oil Process by Axens North America

Go To: Publications Patents

Process Name: H-Oil Process

Company: Axens North America, Princeton, NJ

French Public Company

Website: http://www.axens.net

Process Overview & Objective: The H-Oil Process is a catalytic hydrocracking process which utilizes an ebullated-bed reactor. The process is nearly identical to the LC-Fining Process; H-Oil and LC-Fining share the same early developmental history. The H-Oil Process was commercialized in the 1960's. Currently, there are over 15 ebullated-bed hydrocrackers in operation. The process operates at high pressure and temperature and uses daily catalyst replacement (~1 W% of bed) to a gas/liquid fluidized (ebullated) bed. The catalyst replacement and the nature of the bed allow for fairly high vacuum residue conversion and the production of a product with constant product quality. Ebullated beds are used at the Husky, Shell Canada, and Syncrude Canada Upgraders and operate at 60–75% vacuum residue conversion.

The H-Oil Process can also be applied for partial upgrading of Western Canadian heavy crudes to produce a stable transportable sour SCO. Axens has not published any data concerning this application. As a result, details discussed here are limited. The partial upgrading H-Oil Process will be fed the whole crude or atmospheric residue and operate at low/moderate vacuum residue conversion and at relatively mild operating conditions. The SCO is comprised of the entire liquid product (including unconverted vacuum residue) and distillates from feed fractionation. Process severity is such to insure a stable product and that the typical pipeline specifications (min. 19°API Gravity and 350 cSt at 7°C) are attained. The H-Oil SCO product should resemble a Cold Lake or Lloydminster blend (DilBit) but with slightly lower API gravity and less vacuum residue content.

Claims: The important claims are reduced process severity (pressure, conversion level, catalyst replacement rate) relative to full upgrading designs and the production of a stable sour SCO which can meet pipeline specifications. Hydrogen and catalyst are required. There is no solid (i.e., coke) or heavy liquid byproduct. The total SCO yield from the process will typically be over 100 V% of the feed.

Product & Waste Issues: The H-Oil Process produces significant spent catalyst which can be sent to a reprocesser for metals recovery. The stability of the SCO is the major concern since the blending of light material with the unconverted vacuum residue presents classical incompatibility issues. These issues should have been addressed by Axens.

Scale-up: There are no scale-up issues concerning the ebullated-bed process since it is a mature technology.

Patents: There are many patents related to the ebullated-bed processes; however there are no specific patents or patent applications relating to partial upgrading utilizing an ebullated-bed reactor technology.

R&D Facilities: Axens owns and operates a world-class R&D center in France which includes ebullated-bed pilot units. These units can address any process issues and the evaluation of specific feedstocks and catalysts.

Current Status: Axens is active in Western Canada marketing both the full upgrading and partial upgrading applications of the H-Oil Process. Specific projects are confidential.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the partial upgrading H-Oil Process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
Commercially Demonstrated Process	Process Complexity	Market Valuation of H-Oil SCO
Strong Technical Staff	Requires H ₂ and Catalyst	Compatibility with Other Materials in the Pipeline
No Net Coke Product	Product Stability and Compatibility Concerns	Real Economics for SCO Production
Greater than 100 V% Liquid	Sour SCO with Vacuum	
Yield	Residue	
Additional Development not Required		

The greatest strengths are the extension of a mature, commercially demonstrated technology, the Axens organization and the high liquid yield. The greatest weaknesses are the process complexity, hydrogen and catalyst usage, and the possible issues relative to SCO stability. The latter items should have been the focus of Axens development activities.

Best Applications: The H-Oil Partial Upgrading Process is targeting Western Canadian heavy oil and bitumen to alleviate the need for diluent to transport the crude. The process does not produce significant excess energy and may be more applicable to mining projects versus SAGD. The process economics are directly related to the value of the low API, sour SCO product.

Summary: The H-Oil Partial Upgrading Process can produce a specification partially upgraded SCO from Western Canadian heavy oils and bitumen. The process requires a significant feedrate and a fairly high SCO value to be profitable. Additional technical development is not required. This mature, high yield but

expensive process could be used as a base case to evaluate the technical and economic effectiveness of the other process being investigated.

I^YQ Process

by ETX Systems Inc.

Process Name: I^YO Process Go To: Publications Patents

Company: ETX Systems Inc., Calgary, Alberta

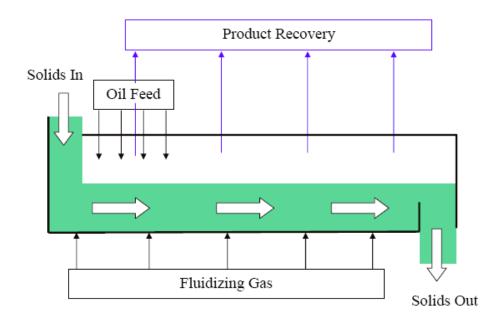
Canadian Private Company

Website: http://www.etxsystems.ca

Process Overview & Objective: The I^YQ Process is a new, developing thermal cracking technology which produces a sour SCO and a coke product which can be oxidized to produce steam and/or power. The I^YQ Process is a partial upgrading process since a small portion of the vacuum residue in the heavy crude feedstock will remain in the liquid product. The process was invented by Envision Technologies (now ETX Systems).

The heart of the I^YQ Process is the cross-flow fluidized bed which is depicted below. The bed of inert solids or coke is vertically fluidized by recycle product gas and moves via gravity, in a horizontal direction. The feed oil (vacuum

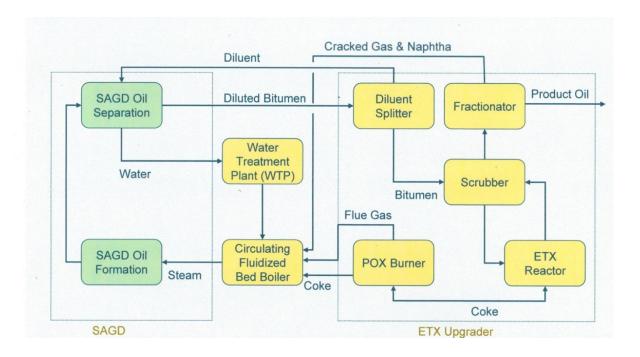
Cross-Flow Coker



residue) is sprayed on the hot solids as they enter the reactor. The oil reacts to form vapor (eventually liquids and non-condensable gas) and coke which deposits on the solid particles. Solid fines are removed from the reactor vapor via cyclones and the condensable vapor is recovered as the product oil. The solids exiting the reactor are now "coked" and are routed to a POX burner and a circulated fluidized-bed boiler to burn off the coke (producing steam) and also for reheating the solids before recycling to the reactor.

The I^YQ Reactor concept is generally similar to the Ivanhoe HTL Process and other technologies such as fluid coking and LR Coking. The I^YQ cross flow fluidized bed has horizontal flow of solids (sand or coke) and a vertical flow of gas. This separates the residence times of the solids and gas. The rates of solid and gas can be optimized to maximize liquids production (minimize gas and coke) and also allows for operation at a lower reactor temperature. This can be a significant advantage over both fluid coking and the HTL Process. Recycle of the I^YQ unconverted residue increases the level of vacuum residue conversion and the API gravity of the net SCO product. The recycle will also decrease the viscosity of the net SCO liquid product.

An overall block flow diagram for an integrated SAGD / I^YQ facility is shown on the following page. The SAGD bitumen is separated from the bitumen/diluent blend in the diluent splitter and sent to a scrubber. The partially condensed product from the I^YQ reactor is also fed to the scrubber. The heavy bottoms from the scrubber are the feed to I^YQ Reactor. Since these bottoms contain unconverted residue from the I^YQ Reactor, a recycle of unconverted reactor product is included in this configuration. The scrubber overhead is sent to a fractionator with the liquid product reported as SCO and the gas and light naphtha routed to the fluidized-bed boiler. The coked solids or coke particles are sent to a POX unit and



combustor for burning the coke and reheating the solids for recycle to the I^YQ reactor. The reason for both a POX and fluid-bed combustor is unclear. Significant steam for the SAGD operation is produced.

Claims: The critical aspects of the I^YQ Technology are related to the benefits from the cross-flow fluidized-bed for coking of the heavy residue. In a fluid bed coker or dilute phase system such as HTL or LR Coking, the flowrates and flow regime (well-mixed or plug flow) of the heat carrier (solid) and fluidizing gas are dependent and are not necessarily optimal. This can result in over-cracking and excessive light gas and coke product selectivity.

The capability of independently controlling the vapor and solids velocities and flow regime limits the thermal chemical reactions before the intermediates can degrade to non-reactive products such as coke and non-condensable gases. A significant claim of the I^YQ Process is reduced coke and light gas yields relative to traditional delayed or fluid coking processes.

Based on verbal communication with ETX Systems, the quality of the $I^{Y}Q$ liquid products is similar to the feedstock fractions. With just a small quantity of remaining unconverted vacuum residue, the blended liquids (SCO) can meet typical pipeline specifications (19° API min. and 350 cSt viscosity max. at 7°C).

The heat carrier used to heat the feedstock and provide a surface for coke deposition is either sand or process produced coke. Long-term tests are required to adequately assess the equilibrium fluidization characteristics of the carrier as it builds up coke and metals and goes through multiple thermal cycles.

In January 2010, ETX announced a new reactor deign for the IYQ Process specifically for the larger scale planned field unit. The design was a result of a collaboration of nozzle designer, engineering and industrial research firms. The details were not revealed although the design is reported to be more compact.

Product & Waste Issues: The I^YQ Process produces a heavy hydrogen deficient liquid product, spent lime (gypsum) from the fluidized-bed boiler and a combustion flue gas. Because of the use of the lime, the flue gas should be an acceptable effluent. The gypsum product may present a disposal issue depending on the plant location.

ETX claims that the liquid product will be more stable and of better quality than that from a delayed coker. This a result of the lower temperature operation and shorter residence time of the conversion products in the I^YQ Reactor. There are no published data to support this claim; however from a chemistry/kinetic standpoint, the I^YQ liquid product should be more stable than that from a delayed or fluid-bed coker. It is noted that the I^YQ Process optionally routes the product light naphtha, which has a high propensity for instability, to the fluidized-bed boiler instead of

including with the product SCO.

Scale-up: The I^YQ Process has not been commercialized. Small-scale laboratory

experiments were conducted to confirm the process viability. A one BPD pilot

plant was started-up in 2009 and is currently operating. Preliminary results have

been published at the 2009 NCUT Conference in Edmonton. The pilot unit will

provide additional optimization and scale-up opportunities.

The scale-up from the 1 BPD pilot plant to the planned demonstration facility

(2,000 BPD) is a large step, particularly considering that the pilot plant did not

include the coke burn off step and the use of recycled solids.

Patents: ETX Systems was granted a Canadian patent in September 2006. This is

the only I^YQ patent and no new patent applications were found. The patent has

not issued in the U.S., however the U.S. patent application appears to remain

active. The Canadian patent is well written and comprehensive in terms of a

theoretical explanation of the benefits of the cross-flow fluidized-bed but does not

contain data on process yields and product qualities. The patent is instructive as to

the design of the reactor and the required operating conditions.

R&D Facilities: Small-scale experiments were conducted (laboratory unknown)

to confirm the process viability. Based on these data, a 1 BPD pilot unit was

constructed at the NCUT laboratories in Edmonton. The pilot unit was funded, in

part, by Canadian governments. The unit construction was completed in 2008 and

after several initial commissioning tests, initial data has been obtained in 2009.

The unit does not include the coke burn off step and utilizes nitrogen as fluidizing

gas. Cyclones are included to remove fines from the reactor effluent.

A 2,000 BPD integrated demonstration plant is planned (pending funding) for a 2011 start-up.

Current Status: The highest level of activity is the start-up, initial operations and possible required modifications to the NCUT pilot plant. Additionally, ETX is active in securing funding for the planned demonstration plant. Land for the demonstration unit has been purchased in Belle Plaine, Saskatchewan. As mentioned above, a new, more compact reactor design was developed in 2009 and announced in early 2010.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the I^YQ Process are shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Good Technical Patent Discussion	No Data in Patent	Why Patent not Issued in U.S.
Sound Technical Approach	No Long-Term Testing with Recycled Solids	Degree of Recycle to Meet SCO Pipeline Specifications
Planned Commercialization Path	Small Newly Founded Organization	Process Scale-up
Strong Technical Staff- Excellent Publications	Product Stability Concerns	Economics for SCO Production
No Catalyst and H ₂ Required, No Net Coke Product	Small Scale Pilot Plant – No Coke Burn Off	Capability of Processing Very Heavy Crude
Fits with SAGD Projects	Long Development Path (>4 Yr)	

The greatest strengths are the sound technical approach, resulting in enhanced liquid yields and quality, the strong technical staff, and that the process fits well with a SAGD project. The greatest weaknesses are the lack of an integrated demonstration of the process, the potential for unstable liquid product, and the long required development time.

As with similar thermal cracking type partial upgrading processes, the final process profitability when using the recycle mode of operation and producing a large quantity of energy are also questionable.

Best Applications: The I^YQ Process is a developing partial upgrading technology which produces significant excess energy and is thus most applicable to SAGD operations. A field application at or near the SAGD site is also preferred since the process does not require hydrogen and catalyst and could possibly generate power.

Summary: The I^YQ Reactor concept has potential for eventual commercialization. This is based on the sound ETX technical approach and on information (not data) from the process developer that the process can produce a specification partially upgraded SCO from Western Canadian heavy oils. The stability of the final thermally cracked SCO is questionable although the I^YQ Process does not include the possibly unstable light naphtha.

JetShear Process

by Fractal Systems Inc.

Process Name: JetShear Process Go To: Publications Patents

Company: Fractal Systems Inc., Sherbrooke, Quebec

Canadian Private Company

Website: http://www.fractalsys.com

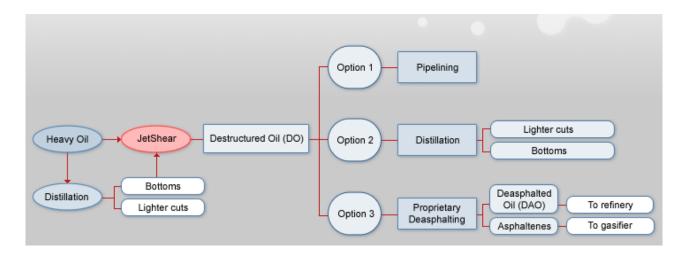
Process Overview & Objective: The JetShear Process is a new version of a thermal viscosity reduction process. The process utilizes a high-shear nozzle which produces kinetic energy via the collapse of bubbles (cavitation), resulting in thermal cracking. The process does not appear to be completely developed. The JetShear product will still require diluent for transportation and will not meet Canadian pipeline specifications. The process is a partial upgrading process since a fairly large portion of the vacuum residue in the heavy crude feedstock will remain in the liquid product. Fractal Systems is a newly formed (2006) private company (Sherbrooke, Quebec,) which is involved solely with the development of the JetShear Process.

The precursor of the JetShear Process was originally developed in the 1980's via R&D funded by Natural Resources Canada (NRC). Based on this work, a patent was issued in 1992. At that time, the process utilized a blend of heavy oil and gas (nitrogen or hydrogen) which was processed through the high-shear nozzle. Pressure and temperature are fairly high. The emphasis or process objective was on heavy oil viscosity reduction, not on cracking or upgrading. Beginning in 2004, additional process development was initiated by Fractal Systems and resulted in the current JetShear Process. As described in the recently issued Fractal Systems patent application, the current process utilizes a paraffinic solvent (e.g. pentane) which is blended with the heavy oil before passing through the shearing nozzle.

The process is non-catalytic, uses no hydrogen, and claims density and viscosity reduction via the use of a high-sheer nozzle through which the heavy oil is processed.

Paraffinic solvent may or may not be included with the heavy oil feedstock. If solvent is utilized, Fractal claims that a filter can be utilized to remove precipitated asphaltenes. Organic liquids mentioned are pentane, butane and alcohols. The organic liquid feedrate is 5 to 25 V% of the total blended feed. This indicates that some deasphalting is occurring in the process and may be the key element of the recent Fractal Systems Process developments.

A simplistic overall block flow diagram for JetShear Unit is shown in the figure below. The diagram does not indicate that a paraffin or organic liquid is utilized



prior to the JetShear reactor as described in the patent application and only the residue from the heavy oil is processed through the nozzle. This is not feasible. Additionally, the figure indicates three possible process configurations with 1) the product sent directly to the pipeline; 2) the separate light and heavy product produced via distillation; and 3) the use of proprietary deasphalting to produce a deasphalted oil (DAO) and asphaltenes for gasifier feed. The diagram may be overly simplistic and attempting to cover all possible applications of the JetShear device.

Claims: The critical aspects of the JetShear Process are related to the benefits from thermally cracking at low temperature. These benefits minimize or eliminate

over cracking of the heavy oil which can lead to high light gas yields and coke production. The process claims heavy oil viscosity reduction such that the required quantity of diluent (for pipeline transportation) can be reduced by 50–90%.

There are conflicting levels of API gravity improvement and viscosity reduction claimed by Fractal Systems. This may relate to the different JetShear Process operating modes (i.e., with/without solvent) or to a developing technology. A summary of these API and viscosity claims is shown in the table below.

	Website	Patent App
API Improvement, °	2.5	2 - 9 ¹
Viscosity Reduction, %	86	0 - 941

^{1.} Lower end of range if solvent included in treated product, higher end of range if solvent is removed

In particular, the Fractal patent application indicates that a 12°API heavy oil (Lloydminster) can be upgraded to 20.6°API with a 610 cPs viscosity at 15°C. This data may indicate that the process can attain the minimum required pipeline API gravity of 19° but is not able to attain the required viscosity (~150 cSt @ 15°C). However, the patent application claims related to API improvement are questionable since without hydrogen addition, it is not possible to attain 8.6°API improvement without either:

- Rejecting a low API liquid or solids product which is hydrogen deficient (e.g. coke or asphaltenes). This will result in a moderate or low net yield of treated liquid product (SCO).
- 2. Including the light (93°API) pentane solvent utilized in the experiment in the "treated" product. The experiment discussed in the patent application processed the heavy oil plus 15 V% pentane through the JetShear device. The JetShear product analyzed appears to be the treated heavy oil plus the

very light pentane. This total product (i.e., including pentane) API gravity claim of 20.6° would result in a misleading conclusion. Inclusion of the pentane solvent in the final product is not realistic since the pentane is light (volatile) and expensive. Additionally, the heavy oil asphaltenes not associated with the pentane will form a separate phase and the net product would be unstable.

At the conditions utilized in the current process and with the inclusion of a paraffinic solvent in the feed, there will be some asphaltenes which will not be soluble in the reactor product. It is not clear, or is it discussed in detail in the Fractal Systems literature, how the JetShear Process will separate the solvent, the precipitated asphaltenes and the heavy oil product from the JetShear reactor effluent. A filter is mentioned; however this is not a feasible commercial solution. Additionally, a critical aspect of any deasphalting technology is the recovery of the solvent which is highly energy intensive. Commercial SDA technologies utilize super and opti critical recovery methods which result in good recovery and minimal operating costs. The use of a paraffinic solvent associated with the high pressure drop shearing of the heavy oil introduces many issues which may have not been completed developed by Fractal Systems.

Product & Waste Issues: The JetShear Process produces a heavy hydrogen deficient liquid product, and if the asphaltenes are burned, a spent lime (gypsum) from the fluidized-bed boiler and a combustion flue gas. Because of the use of the lime, the flue gas should be an acceptable effluent. The gypsum product may present a disposal issue depending on the plant location.

Directionally, the JetShear liquid product will be more stable and of better quality than that produced from a Delayed Coker. This a result of the lower temperature operation and the short residence time of the conversion products in the reactor.

Scale-up: The JetShear Process has been piloted in 1 BPD and 30 BPD bench units. Their website states that they replicated the bench data in a 3000 BPD pilot unit located in Alberta. A 1,000 BPD demonstration plant unit has been fabricated and is ready to be implemented. Scale-up of the process reactor (shearing nozzle) may be difficult. Fractal Systems discusses relatively small modular (skid mounted) units which can be shipped to a site. This may alleviate some scale-up issues. At this point in the process development, scale-up is not a critical issue for Fractal Systems.

Patents: One patent and two patent applications were found relative to the JetShear Process. The patent "Process for Reducing the Viscosity of Heavy Hydrocarbon Oils" was granted in 1992. Esteban Chornet, the Chief Technology Officer of Fractal Systems is listed as one of the inventors. The patent is assigned to the Canadian government and describes a simple system where the heavy oil and a gas (hydrogen or nitrogen) is pressurized and passed though a nozzle or orifice and into a short residence time reaction vessel. The pressure drop across the orifice is 1,000 to 1,200 psi. A U.S. patent application, "Process for Treating Heavy Oils" was published (Sept. 11, 2008) and is assigned to Fractal Systems. The application is closely related to the JetShear Process currently being Considerable time is spent discussing the developed by Fractal Systems. mechanical design of the shearing device. The application indicates that either 100% heavy oil (i.e., no gas) or an organic liquid is processed along with the heavy oil as it passes through the orifice. The latest patent application addresses the boiling curve of the Fractal product compared to the feed.

R&D Facilities: Small scale experiments were conducted in the 1980's to support the NRC patent. This unit appeared to have a capacity of approximately 1 BPD of heavy oil. Fractal Systems operates a 30 BPD bench unit in Quebec, which

according to their website, is available for feedstock testing. The exact configuration and capabilities of the Fractal unit is not provided. The 30 BPD unit is operated for only short time (< 1 hour) as evidenced by a typical experimental test consuming 20 gal or less of heavy oil. No data have been published.

As reported in their website, a 300 BPD pilot unit has been operated and a 1,000 BPD unit has been fabricated. It is possible that these large units operate for very short tests so that expensive feed and product handling facilities are minimized.

Current Status: It is believed that Fractal Systems is still developing the JetShear Process and has fairly recently initiated the introduction of the technology. This is evidenced by the recent website creation and the August 2009 publication. The operation of the 300 BPD pilot unit and fabrication of the 1,000 BPD Unit indicates a high level of activity in the past year or more.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the JetShear Process are shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Simple Process	Not Fully Developed	Preferred Process Configuration
Pilot (Bench) Unit Available	May Not Completely Eliminate Diluent	Process Scale-up
Patent and Patent Applications	Small Newly Founded Organization	Process Economics
No Catalyst and H ₂ Required	High Temperature and Pressure Required	Disposition of Asphaltenes
Low Water Usage	Long Development Path (>4 Yr)	Product Stability
300 BPD Pilot Unit Operated		Data from 300 BPD Unit
1,000 BPD Unit Fabricated		

The greatest strengths are the relatively simple process, claimed low water usage, and availability of the pilot unit. The greatest weaknesses are that the process is not fully developed, may not completely eliminate the need for diluent and requires high temperature and pressure. The latter will adversely affect the process economic feasibility. There are many unknowns concerning the JetShear Process including the preferred process configuration, scalability, and final product stability and compatibility.

Best Applications: The JetShear Process is a developing partial upgrading technology which does not require hydrogen or catalyst and is looking to commercialize the process using skid-mounted commercial modules. It is most applicable to field application and may fit in with SAGD operations if the asphaltene product is burned to produce the steam required in SAGD. Given the current Fractal Systems claims however, the process may not be capable of completely eliminating the diluent required for pipeline transportation. This will greatly reduce the attractiveness of the process to heavy oil producers.

Summary: The JetShear Process is a novel thermal cracking type technology which is not fully developed and may or may not have advantages over the similar CPJ Process which is further along in the development path. The original process patent was issued in 1992 and the technology may have significantly advanced by Fractal Systems, although the final process configuration is not definitive. Since the process does not completely eliminate diluent, it may not be applicable to the partial upgrading route currently being investigated by many heavy oil and bitumen producers.

PetroBeam Process

by PetroBeam, Inc.

Process Name: PetroBeam Process Go To: Publications Patents

Company: PetroBeam, Inc., Raleigh, NC, U.S.A.

U.S. Private Company

Website: http://www.petrobeam.com (not active Nov /2010)

Process Overview & Objective: The PetroBeam Process is a new, developing process (primarily a device) which cracks heavy oil with a spray of high energy electrons. The process operates at low temperature and pressure and provides low/moderate conversion and HDS, and viscosity improvement. The PetroBeam Process and similar processes have been termed CRC or cold radiation cracking although LTRC (low temperature) and HTRC (high temperature) are also evaluated in the PetroBeam patent application. It is a non-catalytic process which does not add hydrogen. There is limited available technical information concerning the PetroBeam Process, although there is significant information in the literature (mostly Russian) related to the use of ionizing radiation for cracking petroleum.

In the PetroBeam Process, the heavy oil is heated to a level to adequately flow through the PetroBeam Reactor. In the reactor, the oil is subject to a high energy spray of electrons from a linear accelerator (1–5 MV). The energy from the electrons breaks the various C-C and other bonds. Typically, during this type of treatment, the free radicals formed after bond breakage can recombine to form crosslink bonds and even larger molecules than in the feedstock. As claimed by PetroBeam, the process either breaks the crosslink bonds or prevents them from forming in the first place. The cracked product flows from the reactor and is routed to standard product separation. Both water (possible source of hydrogen) and ionized air (ozone) have been mentioned as pretreatment steps in radiation-type cracking processes.

Based on the available information, PetroBeam has concentrated on the chemistry of the process and less on the engineering of a large-scale commercial unit addressing critical issues such as the handling of the heavy unconverted residue. Given that there is no hydrogen addition, it is difficult to envision how the process could produce stable products at vacuum residue conversion levels of interest. The unconverted residue, as in a thermal cracking process, would be hydrogen deficient and its disposition would be a focus of process developments.

Claims: There has been significant research into the use of radiation (gamma rays, neutrons, electrons) to crack petroleum, particularly in Russia (Kazakhstan). Based on the research results, electron radiation is considered to be the most applicable energy source for petroleum cracking. The energy absorbed is typically measured in kGy (kilo Grays). One Gray is equivalent to 1 J/Kg and is also equal to 100 Rads. The estimated energy absorbed is just 50 KGy (0.008 MM Btu/Bbl), or \$0.10 – 0.15 per Bbl. This does not include the inefficiency in producing the electron beam from the linear accelerator. The cost and size requirements of the linear accelerator are very large, although new design and fabrication developments may have a significant impact on both these issues.

A major problem with the irradiation of petroleum is the recombination of cracked molecules (crosslinking) and the production of products more viscous than the feedstock. This effect is sometimes desirable for other irradiation applications but is completely in opposition to the PetroBeam upgrading process objectives. The major claim of PetroBeam is that they have developed techniques for either preventing crosslinking (i.e., polymerization) or for breaking the crosslinked bonds. The technique and/or apparatus for accomplishing this is unknown and a key secret for PetroBeam.

The PetroBeam patent application provides a wide array of experimental data with feedstocks generally lighter than the Western Canadian heavy oils and bitumens of interest and does not adequately address the quality and stability of the heaviest product. In some patent application examples, a "coke" product is reported. Although PetroBeam assesses the stability of products via gravity changes after long-term ambient storage, it is unknown if the unconverted residue is included in the stability study. Regardless, the residue may be a condensed solid and would not indicate any storage changes; this does not reflect the issues which would be evident in a commercial PetroBeam processing facility. The numerous publications by Zaikin and Zaikina (now PetroBeam researchers) may address the process yields; however the publications are not readily available (Russian). Based on PetroBeam publication No. 1 (See *Attachment 1*), the studies were not definitive in nature.

Water may be used as a source of hydrogen since the high energy radiation will split oxygen-water bonds. Ozone addition is mentioned in a few technical publications but primarily as a method of sulfur removal, independent of any radiation effects. Bubbling ionized air into the feed will produce water soluble sulfones even at mild operating conditions. The ozone is generated from oxygen (air) via irradiation.

PetroBeam does not provide any data on the yield and quality of the cracked product oil. With no external hydrogen added, claims of producing a pumpable SCO are questionable. Without hydrogen addition, it is not possible to attain 10°+API improvement without rejecting a significant quantity of low API liquid or solid product which is hydrogen deficient (e.g. coke or asphaltenes). This would also result in a moderate or low net yield of final treated product (SCO). Only if there is significant hydrogen consumption via water dissociation can a full

range acceptable SCO product be made.

Given the potential of high energy irradiation, and possible water dissociation, the

production of a pumpable SCO, without inclusion of the unconverted residue, is

feasible. However, the SCO stability and overall yield, the disposition of the

unconverted residue, and the process economics are in question.

Product & Waste Issues: Although PetroBeam has announced that they have

solved the crosslinking issue, the product may still resemble that from a thermal

process like coking. Even if there is hydrogen capping due to possible water

molecule splitting, the degree of saturation at low hydrogen partial pressure will

be minimal. The heavy portion (unconverted residue) of the PetroBeam product

may be heavier and more contaminated that the feedstock and will have a large

potential for instability. The products and equipment will pose no issues relative

to radioactivity.

Another issue for a site located, partial upgrading application is that the process

will produce a sour fuel gas which when combusted will require treatment to

remove sulfur containing compounds. The possible use or generation of ozone is

another safety related issue.

Scale-up: The PetroBeam Process is continuous and since electrons do not

penetrate deeply into a material (~ 3 inches), scale-up may be difficult. Most

probably, modular units of 1,000 BPSD or less will be utilized. A single electron

beam source will be utilized even for large (>10,000 BPSD) commercial size

units. PetroBeam has announced that they have constructed and are (April 2010)

in the process of completing a 1,000 BPD demonstration facility which will

utilized for scale-up studies. The PetroBeam Process scale-up will be a major hurdle.

Patents: A Canadian patent application by two of the PetroBeam scientists was filed in December 2005 (published June 2007) and was assigned to PetroBeam. The same application was recently (March 2010) published in the U.S. The husband/wife team of Mr. Zaikin (PetroBeam's R&D Director) and Ms. Zaikina (Chief Research Scientist) has an extensive publication record and are considered worldwide experts in the field of irradiation processing. The patent application is a scientific-based introduction to radiation cracking with data on the effect of pretreatment, radiation power and dose, and feedstock quality. Storage stability via long-term storage and changes in gravity is addressed. Most of the feeds evaluated where significantly lighter than the Western Canadian oils of interest. It was not clear if the stability of the unconverted residue was adequately evaluated.

R&D Facilities: PetroBeam, Inc. corporate offices are located in Raleigh, North Carolina and the R&D laboratory and the new 1,000 BPD demonstration plant are located in Englewood, NY. A 75 BPD pilot plant has been operated to obtain initial data. According to the PetroBeam website, this unit has been utilized to establish a "proof of concept" with work completed by the end of 2009.

PetroBeam originally announced that the 1,000 BPD demonstration plant will be tested in late 2008, although as of April 2010, there are no updates that the unit was commissioned and started-up. The cost of a unit this size which could operate for an extended period (days/weeks) is well beyond the level of PetroBeam financing. It is therefore assumed that the unit will operate at high feedrate (1,000 BPD = 42 Bbl per hour or 0.7 Bbl per minute) but for a relatively short durations. Depending on the unit configuration, process performance and yields from a short-

term demonstration may not be an adequate representation of expected commercial operation.

Current Status: PetroBeam, Inc. was created in 2005 and has been active in the past few years in publishing their website, initial press coverage, and financing and constructing a demonstration plant. To date, they have raised nearly \$10 MM including \$6 MM from the Ion Beam Application SA (IBA) agreement. Highlights from the website and other public sources are itemized below:

- 1. <u>Demonstration Unit</u> The PetroBeam website originally announced that the 1,000 BPD demonstration plant will begin testing in late 2008. The latest information is that the demonstration unit will be operating by the end of 2009; as of April 2010 there is no update on the schedule. The demonstration unit is a large step for advancing the process, however as discussed above, it is expected that a specific test will be of short duration.
- IBA Sale In January 2008, IBA (Ion Beam Applications), a Belgium manufacturer of electron beam accelerators, acquired a 10% stake in PetroBeam with warrants to extend to 20%. The transaction was for \$6 MM. In return, PetroBeam must purchase all of its accelerators from IBA.
- 3. **Recent Feed Evaluation** Based on sources, PetroBeam is currently active in evaluating crude and heavy oil samples from potential clients. This work was conducted in the small-scale pilot plant.

Strengths / **Weaknesses** / **Unknowns:** A table summarizing the strengths, weaknesses and unknown factors of the PetroBeam Process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
Mild Operating Conditions	Newcomer to Upgrading	Yields and Product Qualities
Strong Scientific Technical	Permitting & Size Requirement	Role of Ozone and Possibly
Team	of Linear Accelerator	Water Dissociation
No Catalyst / Hydrogen	No Available Process Data	Coke Yield & Product
		Stability
Demonstration Plant under	Low HDS	Actual Energy Consumption
Commissioning		Actual Energy Consumption
IBA Sale	Sour Gas Product will Need to	Investment Cost– Particularly
	be Treated	Linear Accelerator
	Small Scale Modules	Demonstration Plant Test
		Duration

From a technical standpoint, the greatest strengths are the new demonstration plant (possibly under commissioning), the mild operating conditions without hydrogen and catalyst, and the strong scientific team employed by PetroBeam. The greatest weaknesses are the lack of supporting data, possibility of the production of unstable products, and the large footprint and investment cost for the linear accelerator. Even with the demonstration plant, the process is in the early developmental stage, particularly from an engineering standpoint, and many years from commercialization. The in-place financing and possible current commissioning of the demonstration plant is a major factor and an indication that the PetroBeam Process has some possible technical and economic merit.

Best Applications: The current PetroBeam target market is for heavy oil conversion. Industrial research has been applied to VGO and atmospheric and vacuum residue streams. Theoretically, radiation can be used to crack any petroleum, for example to replace a FCC Unit. Given the current state of development and questions concerning product stability and the disposition of the unconverted residue, it is not clear what the preferred application of the PetroBeam or similar technology should be.

Summary: Even after more than 15 years of research, the PetroBeam Process remains a developmental technology whose final potential is unknown. The PetroBeam approach is unique and the cracking of heavy petroleum is possible. It is the product stability, disposition of unconverted residue, and engineering design which is in question. The operation and results from the 1,000 BPD demonstration plant will be critical to the future of the technology.

PetroSonic Heavy Oil Upgrader by SONIC Technology Solutions Inc.

Go To: Publications Patents

Process Name: PetroSonic Heavy Oil Upgrader

Company: Sonic Technology Solutions Inc., Vancouver, BC

Canadian Public Company

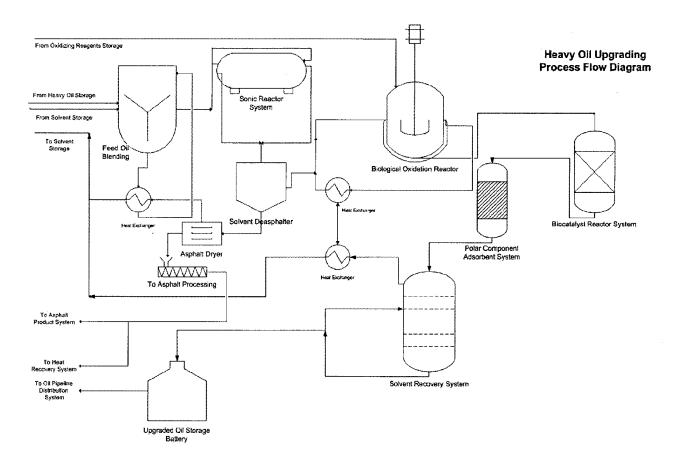
Website: http://www.sonorenergy.com

Process Overview & Objective: The PetroSonic Heavy Oil Upgrading Technology is a new, developing partial upgrading process which produces a full range (contains vacuum residue) sour SCO and an asphaltene product. The process utilizes solvent deasphalting, low frequency sound energy and biotreatment/oxidation technology and claims to produce a SCO meeting typical Canadian pipeline specifications. The asphaltenes can be combusted to produce steam and/or power.

The process combines the features of the original Sonic Technology Solutions (Sonic) Sonoprocess Technology (vibration/sound energy for intimate mixing and faster reaction kinetics), PetroSonic's Heavy Oil Technology, and Northern Oil Research Technologies Inc. (NORT) B²U Process which is a combined deasphalting, bio-treatment/oxidation technology. In April 2008, Sonic acquired NORT for \$3 MM and also acquired 100% ownership in PetroSonic and is currently developing the combined heavy oil partial upgrading process. The new process is currently called the PetroSonic Heavy Oil Upgrader Technology.

The PetroSonic Upgrader utilizes a low-tech, "rapid" deasphalting process with the resulting DAO further treated using bio-catalyst, bio-material and an oxidizing agent to produce a transportable SCO. Octane and meta-xylene are mentioned as the preferred solvents in the NORT patent application, however pentane, hexane and iso-octane are listed as preferred solvents in the 2009 Sonic patent application. The sonic generator is utilized to enhance both the deasphalting and oxidation steps.

A flow diagram from the 2009 Sonic patent application is shown below. The heavy oil (no prefractionation) and non-polar solvents are fed to the Sonic Reactor. Solvent to oil ratios of 0.9 to 3.5 are discussed in the 2009 patent application. It is claimed that the sonic energy enhances the solvent extraction of the non-asphaltenes from the heavy oil through enhanced mass transfer. The product from the sonic reactor is sent to solvent deasphalter separation vessel. The asphaltenes are sent to drying with recovery of the deasphalting solvent. The ultimate disposition of the asphaltenes is not discussed.



The deasphalted product (DAO) and solvent from the deasphalter is optionally treated in the biological oxidation and biocatalyst reactor systems to remove additional contaminants. The biological agents contain enzymes from materials such as peat moss and peanut hulls and catalytically oxidize the contaminants in

the DAO. A chemical oxidation step may be used using ozone or hydrogen peroxide to further oxidize the contaminants. The regents and adsorbents are then filtered from the DAO solvent oil. Finally, the solvent is recovered via atmospheric distillation and the upgraded product sent to storage and eventually to the pipeline.

An October 2008 press release (see *Attachment 1*) from Sonic shows encouraging data based on the processing of Lloydminster heavy oil (10.7°API). The API gravity of the oil product (SCO) is reported as 23 to 28° with approximately 40% sulfur removal. The required Canadian pipeline viscosity specification also appears to be attained. The reported SCO yield is 89.8 V% with a yield range of 85–92 V%. If these results are based on the Sonic patent application SimDist data, however the product sample contains significant unrecovered solvent. Accounting for the high API gravity of the pentane solvent would indicate much lower API gravity improvement (+7°API or an 18°API SCO). This is near the expected API gravity for a DAO product from a pentane deasphalting plant.

If representative of the actual solvent-free product, these data are supportive of attractive process, although data for Athabasca bitumen, which is a more difficult feedstock to upgrade, would be desirable. From other tables and the patent application, asphaltene yields of 12 to 20% W% are apparent. This could be attractive for a field Upgrader for providing the required SAGD steam. The issue of the asphaltene disposition is a primary concern.

Claims: The important technical claims regarding the PetroSonic Heavy Oil Upgrading Technology are enhanced solvent deasphalting as a result of the sonic treatment and the environmental attractiveness of the biological treatment step. No data are provided (i.e., patent or patent applications) to support the claim that

the sonic treatment enhances the solvent extraction step. Comparable data with and without the sonic treatment are required. Other important issues concern the type of asphaltenes which are removed from the feed (solvent used and type of extraction device utilized), the effective recovery of the deasphalting solvent, and the effectiveness of the sonic and bio-treatment of the resulting DAO product.

The critical aspect of any deasphalting technology is the recovery of the solvent which is highly energy intensive. Commercial SDA technologies utilize superand opti-critical recovery methods which result in good recovery and also minimize operating costs. For producing a partially upgraded, transportable SCO, incomplete deasphalting performance (i.e., asphaltenes left in DAO) is acceptable, however high solvent losses (costly) and high energy costs may result.

Low frequency sound energy has been utilized to facilitate mixing and chemical reaction rates. A competitive heavy oil upgrading process (Sonocracking) partially started-up a commercial plant in the Middle East and has been experiencing many issues. A prior Colyar Consultants analysis indicated that the sonic energy was affecting the portion of the crude in the vacuum gas oil boiling range (650-975°F) and not the heavy vacuum residue or asphaltenes. The scale-up of this type of technology in a continuous process and the possible high operating cost are a critical concern.

The use of a bio-catalyst and an oxidizing agent to perform some level of hydrocracking and sulfur and nitrogen removal has been discussed for many years but has limited commercial application. Most of the proposed applications are on lighter boiling range feedstocks (e.g. diesel). Typically, long residence times (large vessels) are required. Additional research concerning this aspect of the PetroSonic Upgrading Technology is required once the development has

progressed and more details of the technical approach are made public.

Product & Waste Issues: The PetroSonic Upgrading Process produces a sour

SCO which will contain deasphalted oil (DAO) and the distillates from the heavy

oil feedstock. There should be no stability or compatibility issues concerning the

SCO since the asphaltene content will be minimal. If the asphaltene product is

burned to produce steam, there will be spent lime (gypsum) from the fluidized-bed

boiler and a combustion flue gas. Because of the use of the lime, the flue gas

should be an acceptable effluent. The gypsum product may present a disposal

issue depending on the plant location.

The use of bio type reagents may present a disposal issue. There are currently

insufficient data to make an assessment of this possible issue.

Scale-up: The PetroSonic Upgrading technology has not been commercialized. It

appears that only relatively small-scale experiments have been conducted. There

may be scale-up issues when the planned field pilot plant starts-up.

Scale-up issues relating to the PetroSonic Technology include: 1) proper and

economical extractor and solvent recovery designs, 2) sonic energy device scale-

up, which is difficult and may result in a modular type unit design, 3) filtration of

the agents and adsorbents in the bio-treatment step, and 4) unforeseen issues

relating to the bio-treatment step which typically requires good contacting and

long reactor residence times. As more information and further development

proceeds on the biological oxidation step, a more thorough discussion can be

developed.

Patents: Sonic has issued several U.S. and Canadian patents and patent applications concerning the sonic device and its application in the environmental field. A recent (September 2009) Sonic patent application filed internationally (not available in the U.S. or Canadian websites) is instructive for the current PetroSonic Upgrading Process and is the basis for much of the discussion above.

The patent application describes the process and provides the results of several

small-scale experiments. Simulated Distillation (SimDist) curves are provided

showing the boiling characteristics of both the feed and products. The product

distillations indicate significant quantity of solvent (low boiling point) material in

the product. This may or may not have been properly accounted for in the Sonic

claims. Regardless, the SimDist data are not representative of the commercial

product which would be attained.

A 2006 U.S. patent application was filed by Fred Boakye concerning the B²U Process. Interestingly, the patent application was not assigned to NORT. The B²U application is instructive as to the scientific basis for deasphalting and bio and chemical treatment of the DAO. The patent is not informative from the

standpoints of process yields, commercial application, process/device scale-up,

and economical feasibility.

R&D Facilities: Both PetroSonic and NORT have developed data based on

laboratory or small-scale pilot plants. The feed capacity of these laboratory units

is unknown. Sonic is planning to build an integrated field pilot plant. The scale of

this unit is on the order of 1,000 BPD as indicated by both the Mirex Energy and

Albanian projects discussed below.

Current Status: Listed below are some of the key items taking place at Sonic

relative to the PetroSonic Heavy Oil Technology:

- 1. <u>Albanian Joint Venture</u> In February 2010, Sonic announced a joint venture with a private Albanian firm to construct and operate the first PetroSonic heavy oil upgrader. The stated capacity is 1,000 BPD and will operate on Albanian heavy crude. Only the first phase (deasphalting step with sonication) will be initially constructed. As a result of existing infrastructure and equipment, the reported cost is just \$1 MM or \$1,000/BPSD. The project ownership is 60% PetroSonic and 40% Albanian.
- 2. Agreement with Mirex Energy Inc. In June 2009, Sonic entered into a 50/50 joint venture agreement with Mirex to build a 1,000 BPD PetroSonic Upgrader field pilot (demonstration) unit. The plant will be located near Lloydminster. Mirex is a private company providing oil services in the Lloydminster area. Mirex has diverse operations and interests including oil production and oil field operations and services. As a result of low margins in Alberta, this project is delayed and Sonic is now concentrating on the project in Albania.
- 3. <u>Patent Applications 2008/2009</u> Experimental data were obtained on the processing of Lloydminster and other heavy oils to confirm the technology and to support the latest patent application. The data appear to be based on small scale and possible separate processing in the NORT and PetroSonic/Sonic laboratories.
- **4.** <u>Technology Mergers</u> Both the NORT B²U Process and the rights to the PetroSonic Technology were acquired by Sonic Technology Solutions in mid-2008.

Strengths / Weaknesses / Unknowns: A subjective and very preliminary table summarizing the strengths, weaknesses and unknown factors of the PetroSonic Technology are shown below.

Strengths	<u>Weaknesses</u>	<u>Unknowns</u>
Deasphalting Approach – Stable Products	New to Heavy Oil Upgrading	Data with / without Sonic Treatment
Low Pressure/Temperature	High Operating Costs – Solvent, Sonic Energy and Bio-Agents	Is Bio Treatment Required to Meet Pipeline Specs
No H ₂ Required, No Net	Probable High Asphaltene Yield for	Actual API Gravity
Coke Product	Very Heavy Crudes	Improvement
Low Light Gas Yields	Many Years for Full Development & Commercialization	Solvent Recovery Technique
Mirex and Albanian Projects		Pilot Plant Sizes
Provisional Patents Filed		

The greatest strengths are the deasphalting approach resulting in stable products and the low pressure/temperature utilized resulting in low investment. The greatest weaknesses are the predicted high operating costs, possible low SCO yield for very heavy feedstocks, and the long time required to fully develop and commercialize the process. It is not currently convincing that the sonic treatment has an effective impact on the solvent deasphalting step and that the process can produce a transportable SCO meeting API and viscosity specifications.

Best Applications: If the PetroSonic Heavy Oil Upgrading Technology can produce a +20°API SCO from Western Canadian heavy oils including Athabasca bitumen and can provide a low-value bottoms stream for steam production, then the process is most applicable to SAGD operations. This would require a fluidized-bed type of boiler to burn the asphaltenes and produce steam.

Summary: The PetroSonic Heavy Oil Upgrading Process is of interest since it may utilize low cost solvent deasphalting to produce a fairly light DAO and a minimal quantity of asphaltenes. The specification of non-conventional biological and chemical treatment of the DAO to oxide sulfur and nitrogen is not initially attractive and may not be necessary to produce transportable crude from Western

Canadian heavy oils. The addition of the Sonoprocessing sonic energy device to the deasphalting step may enhance deasphalting but may not be economically feasible. Scale-up of sonic energy and the related operating costs are an issue. Although a 1,000 BPD plant has been announced, the process is considered to be in the development phase and many years from commercialization.

SonocrackingTM by SulphCo

Go To: Publications Patents

Process Name: SonocrackingTM

Company: SulphCo, Inc., Houston, TX, USA

U.S. Public Company

Website: http://www.SulphCo.com

Process Overview & Objective: The Sonocracking Process utilizes a solid catalyst, water, oxidizing agent (peroxide or ether), and high power ultrasound energy to desulfurize diesel and possibly crack/desulfurize heavy crudes. In the early SulphCo work, diesel range material was the most predominant feedstock and a hydrogen peroxide oxidizing agent was utilized. The success of these experiments evolved into a developmental and promotional emphasis on the desulfurization and residue conversion of full-range medium/heavy crudes (e.g. Arab Medium). Today, the oxidative desulfurization of diesel and lighter feedstocks (with ultrasound assist) appears to be the only market targeted by SulphCo.

The Sonocracking Process operating conditions are mild (ambient-50 psi and 50-200°C) and the reactor size (i.e., residence time) appears to be reasonable. For diesel and VGO, the exposure time is 8 to 20 sec. For residue feedstocks, an exposure time of 100–150 sec was claimed to be required. The process is modular in design with each commercial module processing approximately 2,000-5,000 BPD. The process utilizes a relatively large quantity of water.

SulphCo was founded by P. Gunnerman who has been quite controversial relative to his educational claims, business practices and manipulation of the press. A review of many of the news articles in *Attachment 1* with regard to Mr. Gunnerman's character is quite interesting. As of January 2007, Mr. Gunnerman was no longer involved in the management of SulphCo was no longer the board chairman.

The first Sonocracking Unit started-up in Fujairah (UAE) on a heavy crude feedstock. As stated in the numerous SulphCo press releases (see *Attachment 1*), information concerning the unit's status, feedrates, results are perplexing.

Claims: The process operating conditions are mild and as a result, SulphCo claims that the plant investment is low. Prior process claims are low/moderate HDS and significant residue & asphaltene conversion for heavy crudes although there is no supporting data for Sonocracking heavy oil operations. SulphCo claims that the high power ultrasound creates cavitations and micron size bubbles in the liquid. As the bubbles grow, they eventually implode with a great release of energy with local temperatures as high as 10,000°K and pressures as high as 10,000 psi. These severe local conditions can greatly enhance reaction rates. For diesel oxidative desulfurization, the catalyst and oxidizing agent create sulfones and other sulfurcontaining compounds from the thiophenes and other species in the diesel. These oxidation products are denser and more polar compared to the diesel feedstock and can be removed from the via extraction or by a simple water wash.

The early patents indicated that the water requirements for the initial emulsion are as high as one part per part of petroleum feed. This is a significant quantity and therefore water recovery in a commercial facility is thus a required feature. For residue applications, the Sonocracking patents indicated that recycle of the reactor product is required to attain a reasonable level of product quality.

The type of catalyst utilized in the process depends on the type of feedstock. The SulphCo patents indicate that catalyst is held in the reactor by vertical screens through which the feed passes through. There may be several such screens in a given reactor. For diesel feedstock, a tungsten catalyst was originally specified. For heavy crude feedstock, a Fenton-type catalyst may be used. Fenton catalysts

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contain heavy metal ions (Fe, Mn) which in the presence of peroxide create reactive hydroxyl ions. Typical application of Fenton catalysts are in wastewater treatment and for toxic waste destruction. The hydroxyl ions which are created cleave and oxidize organic compounds. Agglomeration of the catalyst on the screens when processing an asphaltenic heavy feed is a large concern.

From one of the more recent U.S. patents, the lightening of the boiling curve as a result of treatment in the Sonocracking Process is illustrated. The feedstock is light whole crude. Only the boiling curves of the feed and product are discussed in detail, yields, product quality and process performances are not revealed. The results are summarized in the table below and show an approximate 20%

conversion of the VGO boiling range material to diesel and naphtha. There is little or no effect on the vacuum residue portion of the feed with just a 1 W% change

Boiling Range, °F	Feed, W%	Product, W%
IBP – 350	8	13
350 – 650	40	44
650 – 975	45	37
975 ⁺	7	6

from feed to product. Since the process includes emulsifying with water and the adding of other organic and inorganic materials, it is difficult to ascertain the exact effect of the ultrasound energy. Regardless, the process is not applicable for the processing of heavy crudes containing high vacuum residue contents (i.e., Athabasca Bitumen).

Based on the above results and possibly the experience at Fujairah, SulphCo appears to have abandoned serious efforts on the application of their technology to heavy crudes (i.e., vacuum residue) and is now concentrating on oxidative desulfurization of diesel and lighter feedstocks.

Product & Waste Issues: For the processing of distillates and VGO, the Sonocracking products should be stable. The disposition of the small quantity of extracted sulfones and other species is not addressed by SulphCo. For heavy feedstocks, there is a large concern for product instability and asphaltene

precipitation.

Scale-up: SulphCo has built and operated 1,000 and 5,000 BPD units at its laboratory originally located in Sparks, Nevada (now in Houston). Additionally, a 2,000 BPD demonstration unit was built and operated by Chevron. The scale-up from these units to a commercial size facility (+10,000 BBSD) should not be an issue since the process design is modular. If reactor sizes become too large, multiple Sonocracking modules could be constructed. SulphCo started-up the first commercial size module (~30,000 BPSD) in the UAE. The stated full capacity will be 210,000 BPSD with seven 30,000 modules (now six modules with total

capacity of 180,000 BPSD).

Patents: Nine U.S. patents have been issued to SulphCo concerning the process or specific equipment designs. Five of the patents concern the ultrasound device and four concern the process and operating conditions. The issued patents discuss mild desulfurization of diesel and do not address heavy oil processing. In addition to the granted patents, four patent applications have been filed. Two of these new

applications concern heavier oil processing.

R&D Facilities: Sonocracking R&D is now conducted at the SulphCo Houston facility which has a 5,000 BPD and a 1-15 gal/hr testing unit. The unit in Fujairah is also available for field testing. The original R&D was located in Nevada which included the 5,000 BPD Sonocracking Unit. Additionally, ChevronTexaco constructed a 2,000 BPD Sonocracker in their Richmond, CA facility with the

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equipment supplied by SulphCo. The Chevron unit operated for some time although no process performance results were ever published. A 2,000 BPD unit has reported to be started-up in Korea, although no data is available. A 5,000 BPD test unit is operational in Europe via a SulphCo testing partner.

Current Status: The recent news concerning SulphCo is all concerning diesel oxidative desulfurization. The company has had bad press concerning technical and managerial ethics yet continues to expand its activities with some possible successes (unit installations) with the process applied to diesel feedstocks. Listed below are the key items currently taking place within SulphCo:

- Agreements with Golden Gate Petroleum and Laguna Development
 Corp In 2009, SulphCo announced agreements with these firms for diesel desulfurization studies and technology evaluation.
- 2. Agreement with OMV In May 2009, SulphCo announced an agreement with OMV (Austrian) which is evaluating the technology for crude oil desulfurization (now only diesel desulfurization). A laboratory scale Sonocracking Unit was shipped to the Austrian laboratory for the OMV evaluation.
- 3. Agreement with Pt. Isis Megah An agreement with this Indonesian oil & gas services company was announced in February 2008. Pt. Isis Megah has rights to sell units in India, Malaysia and Singapore. Sonocracking Units (90,000 BPSD capacity) were shipped from Fujairah to Singapore in March 2008 in response to a 30,000 BPSD "order" and anticipation of additional sales. New management has been installed at Megah and they are reevaluating the Sonocracking decision via testing in Houston. To date (May 2010), the Sonocracking units remain in storage in Singapore and the Houston testing has not been conducted.

- 4. <u>Pilot and Commercial Tests</u> In 2007/2008 SulphCo performed pilot tests for a U.S. client which were confirmed by field tests at the European testing partner.
- 5. <u>Fujairah</u> The design and construction of an eventual 210 KBPSD unit is underway for this small Arab country. The project is a 50/50 venture of SulphCo and the Fujairah government. Originally the plant was announced to have seven modules, each processing 30,000 BPD. Each 30,000 BPD model is comprised of six 5,000 BPD skids. Recently (2009) the capacity is quoted as 180,000 BPSD (vs. 210,000) and only a small 30,000 BPD facility has partially started-up. A feedstock API gravity increase of 3° and up to 40 sulfur removal has been reported by SulphCo. As noted in Item 1, half of the Fujairah units (90,000 BPD capacity) have been shipped to Singapore. During late 2009, the units do not appear to have been operated.
- 6. MOU's and Agreements In the last three years, SulphCo has signed MOU or testing/marketing agreements with several firms including Petrobras, OMV and Nippon Oil. In some cases these have included the testing of samples in the Sonocracking Process, for others it is simply to execute a Confidentially Agreement and evaluate the process.
- 7. <u>ChevronTexaco</u> The agreement between SulphCo and ChevronTexaco was signed in August 2004 expired in August 2005. After building and operating a 2,000 Sonocracking demonstration plant in the Chevron Richmond refinery, Chevron opted to drop its interest in the technology. No data from the operation were released, implying that the Chevron pilot unit results were not positive.
- 8. Oil-SC A 2,000 BPD demonstration unit was started-up in 2006 in Korea, although no data have been published. The unit is guaranteed to upgrade Arab Medium crude by 9.8 % API gravity (+3°), and to attain 29 W% HDS and 30 W% HDN.
- 9. <u>Total</u> SulphCo has tested bitumen for Total in relation to the Surmont Project in Alberta and exclusive right in parts of Europe. No results

have been released. It is not believed that there is any current agreement between the two firms.

10. <u>Bechtel</u> – In 2001, Bechtel evaluated the SulphCo Process and concluded that it was not commercially viable.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the Sonocracking Technology as applied to heavy oil feedstocks, is shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Unique Process	Large Water Usage	Product Stability for High Asphaltene Feedstock
Low Capital Investment	Recycle Required	Catalyst Poisoning with Heavy Feed
Commercial Projects Initiated	Catalyst Cost and Usage	Plugging on Reactor Screens
No Hydrogen Addition	Minimal Recycle Data	Net Water Usage and Cost
SulphCo R&D and Manufacturing Facility	Low Levels of HDS & API Improvement	
Mild Operating Conditions	No Data on Heavy Oils	
Numerous Patents	Loss of Chevron Project	
	High Operating Cost	

The strongest strengths are the mild operating conditions, patents, and current commercial projects. The strongest weaknesses are the low levels of HDS and API gravity improvement, estimated high operating costs, lack of data on heavy feedstocks, and the failures of Chevron and Bechtel to pursue Sonocracking after a comprehensive evaluations.

Best Applications: SulphCo is current emphasizing the oxidative treatment of diesel and lighter oils with the ultrasound in an assisting role. The prior emphasis was on medium/heavy oil feedstocks and particularly the pretreatment of these

feedstocks prior to standard hydroprocessing. The Sonocracking Process cannot adequately process a solids containing, high asphaltene content heavy oil such as Arabian Heavy or Athabasca bitumen.

Summary: Given the rejection by Chevron and other major technology firms, the current emphasis on diesel feedstocks, the negative press, and the many unknowns concerning the process, I would not consider Sonocracking for heavy oil applications or have any interest in SulphCo. Most importantly, the process, even if technically and economically feasible, cannot provide the level of API improvement and viscosity and sulfur reduction required for typical heavy oil or Athabasca bitumen.

TRU Process

by TRU Oiltech, Inc.

Process Name: TRU Process Go To: Publications Patents

Company: TRU Oiltech Inc.

Sub of Rival Technologies Inc., Las Vegas, NV

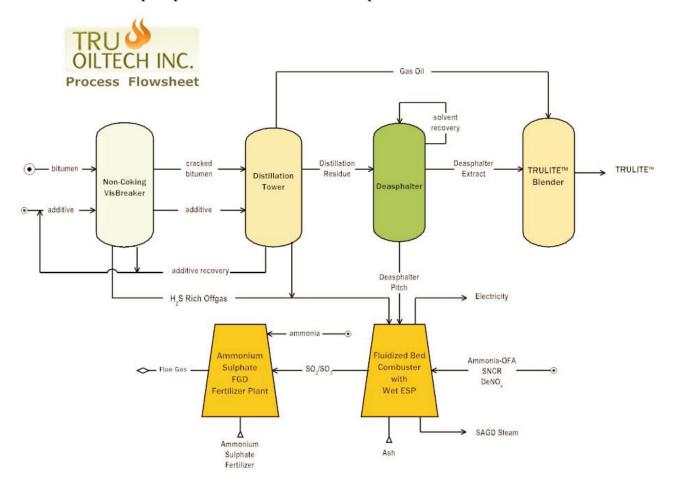
U.S. Public Company

Website: http://www.truoiltech.com/ (not active Nov /2010)

Process Overview & Objective: The TRU Process is a developing partial upgrading technology which uses a recyclable distillable additive (thermal reagent), a visbreaker reactor, atmospheric fractionation, and a pentane solvent deasphalter to produce a transportable heavy oil or bitumen. Based on the TRU Oiltech patent application, the thermal reagent is tetrahydrofurfuryl alcohol (THFA). It may aid in reducing visbreaker severity and minimizing olefin production although this is not a published claim in the TRU Oiltech patent application. The process is targeting partial upgrading to allow transportation to an Upgrader or a heavy oil refinery. Press releases claim low HDS, significant API increase and high liquid yields.

The original TRU Process was owned by three individuals including G.A. Constable, its current President. The Canadian process was developed in the 1980's. At that time, process claims of ~15° API improvement (resulting in transportable SCO) were insufficient to warrant further development with the low oil prices experienced in the 1980's and 90's. The original company and the process rights were acquired by Rival Technologies in October 2005 for company stock then valued at just \$40,000. Rival Technologies is a technology development firm and owns another developing technology company related to engine additives. Today, Mr. Constable is President and Klaus Oehr is listed as co-founder and Director of Research and Development at TRU Oiltech. Mr. Oehr is mentioned as a petrochemical innovator although his background appears to be mainly in the environmental field.

A simple process flow diagram for the TRU Process taken from the TRU Oiltech 2008 World Heavy Oil Congress presentation is found below. The THFA reagent is fed to the visbreaker reactor along with the heavy oil or bitumen feedstock. The visbreaker liquid product is sent to an atmospheric distillation column where the



THFA and a naphtha / diesel stream are recovered. The THFA additive is recycled to the visbreaker and the naphtha / diesel are sent to SCO blending. The atmospheric distillation column bottoms are routed the pentane deasphalting unit. The DAO from the deasphalter plus the distilled naphtha / diesel oil are blended to produce the final SCO product which is termed TRULITE. The rejected asphaltenes from the process plus the light hydrocarbon and acid gases from the visbreaker are routed to a fluidized-bed combustor to produce steam and optionally power. This may be in-balance with the energy requirements for a

SAGD plant. The combustion gases must be scrubbed or the process must include

limestone addition to remove contaminant sulfur.

There are two variations of the process. TRULITE LD corresponds to 10% (W%

on feed) THFA addition; TRULITE HD corresponds to 20% addition. A THFA

recovery of 99.5 % is claimed. Therefore for a 25,000 BPSD facility, TRULITE

HD production would require 8,850 Lb/Day of make-up. At a THFA unit cost of

\$1.00/Lb (2003), the net additive cost is approximately \$0.35/Bbl of heavy oil.

Based on this, lower solvent recoveries (e.g. 95%) would be detrimental to the

process economics.

An analysis of the 2008 World Heavy Oil Congress presentation indicates a high

visbreaker conversion (~40%) and high API conversion products. The latter is not

possible without hydrogen addition or the inclusion of a light material in the

product. At present, there is insufficient published information to adequately

evaluate the technical feasibility of the TRU Process.

Claims: TRU Oiltech claims that the TRU Process can economically produce

transportable crude (>19°API and <350 cSt viscosity @ 7°C) from Athabasca

bitumen and Western Canadian heavy oils. As will be noted below, recent claims

indicate 86.3 V% SCO yield from Athabasca bitumen, which is fairly high.

Touted as a thermal process, there is no hydrogen addition and no catalyst utilized.

As discussed below under "Patents", the TRU Oiltech THFA additive claims are

not substantiated and no process data with/without the THFA additive are

provided or discussed.

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Process performance claims in the TRU Oiltech press releases include the following, in chronological order:

Mid - 1980's	API gravity improvement from 12 (feed) to 30° (product)
Feb. 8, 2006	67% HDS, 88% acid number reduction
March 28, 2006	High yield at 27°API (feed at 9.3° API), 99% viscosity reduction
July 11, 2006	API improvement (Lloydminster crude) to 27.9° API, 99.9% viscosity reduction, 63% acid number reduction
Feb 26, 2008	Athabasca bitumen feedstock – 86.3 V% yield containing 82.7 V% distillate material (feed has 50 % distillates) and the production of a pumpable product

Without the visbreaker and with no impact of THFA, a blend of Athabasca bitumen distillates and pentane DAO will provide a 14°API SCO. In the TRU Process, the visbreaker conversion products plus the impact of the THFA must therefore provide the additional distillates to increase the API gravity to the SCO pipeline specification of 19°. This would require a high visbreaking severity (conversion) corresponding and a high API gravity of the conversion products. The high visbreaker severity would greatly increase the potential for the production of unstable products. To attain the pipeline API specification, the THFA addition must therefore have a large impact on the process; however, this is not supported in the TRU Oiltech patent application.

Product & Waste Issues: The disposal of the low-value, heavy asphaltene product and the acid gases from the visbreaker are important considerations. TRU Oiltech indicates that a combustor with limestone addition or some sort of scrubbing will be employed to dispose of these two products. This is an expensive solution and will greatly impact the economic viability of the TRU Process. The

stability of the thermally produced light oil product is also in question although with the majority of the asphaltenes removed via deasphalting, the final SCO should be stable.

Scale-up: The small-scale batch experiments at the Alberta Research Council will require significant scale-up. Since the process employs a recycle of the distillable additive, long-term testing of a large-scale pilot unit will be required to insure equilibrium purge rates and realistic yields and product qualities. The 1 BPD continuous unit under design should be of sufficient size to address most of the scale-up issues.

Patents: TRU Oiltech has stated that they have filed two provisional U.S. patent applications. These are not currently accessible via the USPTO; however a single patent application, published in October 2008, was found in the International Patent database. The patent application concerns the mixing and distillation of heavy crudes and THFA solvent. Visbreaking and solvent deasphalting are not discussed.

According to the patent application, the heavy oil /THFA mixing is accomplished at 150°C and sometimes included aeration. The atmospheric distillations of samples with and without the 10% THFA addition were compared and the application claims higher distillate yields with THFA addition. Additionally, the THFA containing samples had lower ASTM D86 distillation endpoints (point of foaming) which TRU Oiltech attributed to enhanced thermal cracking. It is important to note that the THFA (boils at 178°C) was included in the distillate yield reported in the patent application. A quick estimate indicates that the enhanced distillate production was simply due to the inclusion of the THFA solvent, implying that the THFA had no effect on the quantity of distillate yields.

The patent application also contains numerous comparisons of the original heavy oil or bitumen inspections with the TRU Process distillate inspections, claiming greatly improved viscosity and API gravity. These comparisons (of bitumen and bitumen-derived distillates) and claims are meaningless. Based on these issues and discrepancies, it is doubtful if the application will be approved.

R&D Facilities: TRU Oiltech has been conducting small-scale batch pilot plant research at the Alberta Research Council facilities in Alberta. The exact scale is unknown and if corresponding to the published patent application may be on the order of 100 g. Batch type experiments are typically not indicative of continuous results. There are plans for a 1 BPD continuous pilot unit and a larger demonstration facility. An initial pilot plant design has been completed and a \$6 MM cost estimate developed. It is unknown if the pilot plant will include the deasphalting and pitch combustion steps.

Current Status: Listed below are summaries of the important activities at TRU Oiltech in the past few years:

1. BPD Pilot Plant – A design and cost estimate (\$6 MM) for this continuous 1 BPD pilot unit was announced in mid 2008. Construction was to initiate in late 2008 and be completed in mid 2009. Pilot plant units for Ecopetrol and a European client have also been previously announced by TRU Oiltech. In late 2009, TRU Oiltech announced that \$137 MM financing agreement had been secured to build the first pilot plant, demonstration plant and a minimum 10,000 BPD field unit. The financing is though an investment group led by Bridge Gap Konsult of Calgary. The continuous pilot plant would be a major step for the process.

- 2. <u>Ecopetrol</u> In late 2009, TRU Oiltech announced that the South American oil company interested in the technology and in constructing a pilot plant was Ecopetrol (Columbia). As of May 2010, an agreement between TRU Oiltech and Ecopetrol has not been executed.
- 3. Presentation at 2008 World Heavy Oil Congress The first TRU Process publication was presented at this March 2008 conference in Edmonton. Data presented include an SCO yield from McKay River heavy oil at 84-87 V% with an API Gravity in the 18–22° range. A copy of the presentation was obtained from TRU Oiltech and is available from Colyar Consultants.
- 4. <u>Joint Venture Agreement with Venezuela</u> In February 2007, Rival announced a joint venture agreement with Venezuela to commercialize the technology. No details were provided. As of mid 2010, there is no news or update on this JV.
- 5. <u>Pilot Test Results</u> As discussed above, TRU Oiltech has been highly publicizing test results obtained in 2006-2008. These have indicating improving product quality and viscosity reduction, implying significant advances to the technology.
- 6. <u>Rival Technologies</u> TRU Oiltech was acquired by Rival Technologies in September, 2005. At the time TRU Oiltech had three owners, Normal Carlson, Gerald Heelan and G.A. (Sandy) Constable. The press release stated that Rival will fund experimental tests to help commercialize the technology. The purchase price was \$40,000.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the TRU Oiltech Technology is shown on the next page

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Patent Application Filed	Non-Technical Staff	Role of Additive
Reasonable Technical Approach – Not Inc. THFA	Disposal of Asphaltenes	Market Value of SCO
No Catalyst or Hydrogen Addition	Numerous Trivial Press Releases	Product Stability
Pilot Plant Designed	Many Years from Commercialization	Required Investment
Claims that Transportable Crude can be Produced	Poor Patent Application Write- up and Results	Scale-up
Positive Test Results at ARC	Inconsistent Results in 2008	Actual Recovery of
Reported	Publication	THFA and Net Cost
Can Fit with SAGD	Small-Scale Laboratory Results	

The greatest strengths are the fairly simple technical approach, elimination of asphaltenes in the SCO, and that the process is claimed to applicable for partial upgrading of Athabasca bitumen producing a transportable SCO. The greatest weaknesses are the poor patent application, lack of convincing technical data, and predicted high investment cost (asphaltene combustion important).

Best Applications: The TRU Oiltech experimental results on Athabasca bitumen and Lloydminster heavy oil indicate they are targeting Western Canadian heavy oils and bitumen and producing a sour transportable, partially upgraded SCO. Given these data and the high rate of steam production from the combustion of the sour gas and asphaltenes, the process is most applicable to SAGD produced bitumen.

Summary: The overall technical approach of the TRU Process is sound (role of THFA not clear) although based on the single patent application and the 2008 publication, it is not convincing that the process can produce a transportable SCO from Western Canadian heavy oil and bitumen. There are numerous unknowns

and the process is many years from possible commercialization. The published patent application is not encouraging. The operation of the planned 1 BPD is critical to the further development of the process.

Value Creation Group Technology by

Value Creation Inc.

Go To: Publications Patents

Process Name: Value Creation Group (VCG) Technology

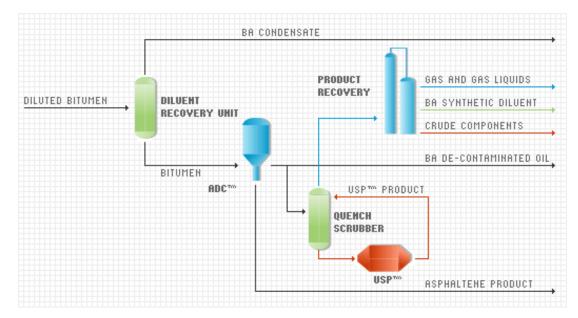
Company: Value Creation Inc., Calgary, Alberta and Hong Kong

Canadian Private Company

Website: http://www.vctek.com/index.html

Process Overview & Objective: The Value Creation Process is a two-step process for producing a medium grade, sour SCO which will not contain heavy residue. It could also be termed a full upgrading process (no residue in SCO) but with no secondary upgrading via hydrotreating, the SCO product will have a relatively low API Gravity of 24 - 28°. Value Creation was founded by Mr. Yeung (formerly of Shell Canada) and is the parent company of BA Energy, the operator of the Heartland Project which initiated construction and is now (late 2009) cancelled. The two steps involve a novel SDA process and a thermal cracking process, both of which are tailored to heavy oil and bitumen. Value Creation had been secretive as to the process details, R&D conducted, and any pilot plant data, although two patent applications were issued in late 2006 and a U.S. patent grated in late 2009.

A block flow diagram for the BA Energy Heartland Project is shown below. The

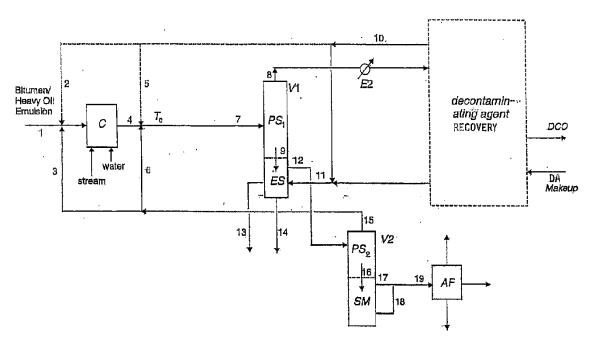


bitumen from the diluent recovery section is sent to the first step called Accelerated Decontamination (ADC). In this first step, an essentially asphaltene-free stream named de-contaminated oil (DCO) and an asphaltene product are produced. The DCO can also be termed a deasphalted oil or DAO. For the Heartland Project, the high sulfur asphaltenes are stated to be sold as fuel. The DCO can be sold as a heavy product (API Gravity ~20°) or sent to the second step, called Ultra Selective Pyrolysis (USP) via a quench scrubber. In the USP Unit, the bottoms from the quench scrubber are thermally cracked with the resulting coke product combusted to provide process heat and to produce steam. The thermally cracked products are combined with the quench scrubber overhead and form the sour SCO product. The partially oxidized flue gas from the USP coke combustion is treated with lime to remove sulfur. The flue gas is routed to a cyclone to remove solids (including calcium sulfate) and then sent to a CO boiler to complete the combustion.

Claims: VCG claims that the process is a low cost alternate to full upgrading since the pressure is low and the difficult to process asphaltenes are removed in the first step. The process is also claimed to be flexible and can produce a wide range of SCO qualities, at the expense of SCO yield (i.e., higher quality SCO = lower SCO yield). VCG claims that the two processing steps involved are novel inventions which are optimized for heavy Canadian feedstocks. There is no hydrogen or catalyst required for the overall process.

A more detailed discussion of the VGC process steps is discussed beginning on the next page.

Step 1 - A flow diagram for the first step (ADC Process), taken from the 2009 patent, is shown below. The primary stated advantage is that asphaltenes can be separated from bitumen using a low solvent to feed ratio and at low pressure and temperature. Additionally, the recovered DCO will contain very low asphaltene content. The process uses a paraffinic decontaminating agent (e.g. pentane or hexane) and water/steam to separate the asphaltenes (heptane insoluble) and light oil (DAO). The bitumen feed can contain water and solids, implying that it could be the froth from a bitumen extraction step. The feed is first conditioned in vessel C with decontaminating agent (DA) after which further DA is added.

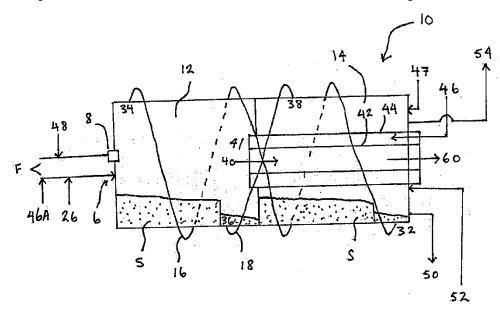


This is followed by two steps of separation to obtain an asphaltene water product (stream 19) and a DAO/decontaminating agent product (stream 8). The latter product requires additional separation to recover the solvent. This last step is energy intensive and can be modeled after the existing supercritical or opti-critical solvent deasphalting (SDA) processes.

Given the lack of published data, it is difficult to technically and economically assess the ADC Process relative to commercial SDA process. However, with construction initiated for a commercial plant (now stopped), one could assume that the process will provide the required yields and product qualities. It is the relative economics of the process which are in question.

The ADC economics would be affected by the possible large vessel size requirements due to treatment of the entire heavy crude stream. In commercial SDA processes, only the vacuum residue portion of the crude is processed. For Athabasca bitumen, the ADC Process feedrate would be nearly twice the feedrate to a commercial SDA Unit. Additionally, commercial SDA Processes operate at elevated temperature and pressure to enhance the separation of asphaltenes. The ADC operates at lower temperature and pressure which could result in long residence time requirements and larger process vessels.

<u>Step 2</u> – A sketch of the VCG USP device (from the 2006 VCG patent application) is shown below. At the Heartland Upgrader, the USP treats the heavy ($\sim 350^{\circ}\text{C}^{+}$) portion of the DCO from the ADC Process. The operation is at near



atmospheric pressure. The device thermally cracks and combusts the resulting coke in a single horizontal rotating reactor system. The device is similar in concept to a rotary kiln used in the cement industry and also to the Alberta Taciuk Processor which was developed over 20 years ago and is in commercial use for retorting oil shale and for soil remediation. The USP device rotates at approximately 5 RPM, is slightly tilted, and moves solids from one side (thermal cracking) to the other (coke combustion) via coils 16 and 18 in the sketch. Feed enters on the left side and contacts very hot solids, entering from location 34, for a short residence time. The solids are ceramic beads of approximately 1 cm in diameter. Coke deposits on the beads' solid surface. The vaporized thermally cracked products are cooled in the annulus (40) in which steam is raised from the combustion flue gas. The coked solids enter the right side of the device at location 38. The coke on the surface of the ceramic beads is partially combusted with air. Make-up ceramic beads plus some finely divided lime can be fed to either the reaction or combustion zones. The lime will absorb the sulfur from the flue gas. The flue gas exits the USP at location 54. The hot ceramic beads are returned to the thermal cracking zone via line 16.

The USP is a novel device which is designed to process low asphaltene and low CCR feedstock and, as a result should have a relatively low coke yield. The VCG patent application claims a low coke to CCR ratio resulting from a short residence time in the thermal cracking section. An alternate explanation is that this may be a result that the feedstock is asphaltene-free and that the coke yield from DCO CCR is lower than that from asphaltenic CCR.

Product & Waste Issues: The VCG Process produces a heavy asphaltene stream which BA Energy indicated could be sold as fuel. This stream has a zero or negative value. Although the Heartland Project may have had a planned

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disposition for this product, it may present a problem in the future and for other

projects. Asphaltenes are solid at ambient conditions, and can contain in excess of

7 W% sulfur and over 1,000 Wppm contaminant metals. Generally, SDA

asphaltenes are not directly usable for the manufacture of road or roofing asphalt.

The process produces a spent limestone product resulting from flue gas treatment;

generally this does not present an issue since the calcium sulfate (gypsum) is used

in the building industry.

The stability of the thermally cracked SCO product is a possible issue, although

this should have been adequately addressed by VCG given that the Heartland

Project construction was initiated. The product from the USP is a thermally

cracked liquid; however, the feed is the ADC DCO product which is claimed to be

essentially free of asphaltenes.

Scale-up: VCG operated a small pilot facility in 2002-2004. Prototype units for

both the ADC and USP steps were operated since 2001. The sizes of the prototype

units are unknown. Due diligence of the technology, including scale-up

calculations, was performed by Purvin & Gertz, R.W. Beck, Inc. and Barnes and

Click, Inc. VCG has not been open concerning the development history of the two

process steps.

Scale-up is not a critical concern for the ADC Process. Scale-up of the USP

Process is a concern since the process involves both liquid solid contacting (scale-

up issue) and a "dirty" mechanical device (maintenance issues). BA Energy stated

that the maintenance schedule for the USP is 18 months, compared to 42-48

months for the USP Process. The similar Taciuk Processor in Australia has had

difficulty in operating consistently.

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The number of USP devices for the 50,000 BPSD Heartland Project is not known. The stated capacity of a single Australian Taciuk Processor, used for oil shale retorting, is 210 T/Hr. Although not directly related, this would be equivalent to approximately 30,000 BPSD of liquid feed.

Patents: Two U.S. patent applications were filed by Value Creation Inc. in November 2006. One patent application covers the ADC Process and the other the USP Process. The application covering the ADC process was granted December 2009. Based on my knowledge of the technology, the patent and application are instructive as to the details of the processes. The patents are well written but do not contain confirming pilot plant data. This may be due to VCG not wanting the process details in the public domain.

R&D Facilities: VCG operated a small-scale pilot unit for demonstrating the second step (USP Process). Larger prototype units for both process steps were constructed and operated since 2001. The ADC unit is located at High River Alberta. The USP unit is located in Calgary. The scale and capabilities of the VCG prototype units are not known. VCG did operate a small-scale pilot unit for demonstrating the second step (USP Process).

Current Status: Value Creation Inc. had developed a stand-alone Upgrader (Heartland Project) using its proprietary technology. This project and some other items are discussed below.

Partnership with BP – In March 2010, Value Creation entered into a partnership agreement with BP to develop the Terre de Grace Project.
 BP will be the majority owner and operator of the project. Ownership of the Heartland Project and Value Creation technologies is not affected

- by the agreement. The application of the Value Creation technology at this project does not appear to be certain since further joint testing of the technology is planned.
- 2. <u>Bankruptcy</u> BA Energy halted constructed on the Heartland Project in September 2008 and filed for bankruptcy protection on December 30. In January 2009, the courts gave BA Energy 90 days to attempt to restructure to avoid bankruptcy. Failing this, the assets of the project were put up for sale in September 2009.
- 3. <u>Terre de Grace Project</u> The latest BA Energy / Value Creation Project is a smaller scope (8,000 BPSD) pilot project will utilize the VCG technologies and the oil sands leases owned by Value Creation. The status of financing for this project is unknown.
- 4. Heartland Upgrader BA Energy Inc. and its parent company Value Creation Inc. developed the Heartland Upgrader Project located in Strathcona County, north of Edmonton. The first phase of three equal phases was to process 54,800 BPSD of Athabasca bitumen (75,000 BPSD including diluent). BA Energy broke ground in September 2005. The EPC contract was awarded to Jacobs Canada with assistance from Larsen & Toubro, Ltd. The primary source of initial funding was investors from Hong Kong; private funds have also been raised for subsequent activities. An IPO was planned to raise additional funds (\$230 MM) but was cancelled in early 2007. BA Energy halted construction in September 2008, filed for bankruptcy protection and finally in September 2009, the project assets were placed for sale.
- 5. Oil Sands Leases Value Creation also owns 16 oil sands leases (218 miles²) containing 10-20 billon barrels of recoverable bitumen. In mid-2004 Value Creation began an initial drilling program. The Heartland Upgrader is touted as a merchant refinery; it is not clear if the recovered bitumen could comprise a portion of the feed to the BA Energy Upgrader. In March 2007, it was announced that Value Creation will begin production and build second Upgrader using oil from their oil

sands leases.

6. <u>PanCanadian</u> - In 2001, Value Creation Inc. signed an agreement with PanCanadian (now EnCana) to jointly advance oil sands upgrading technology. The terms of the agreement were never disclosed and it is possible that the agreement has expired.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the VCG Process is shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Strong Technical Staff and	Questionable Compatibility /	Rotating Equipment (USP)
Company Founder	Stability of Liquid Product	Maintenance Cost
Claimed Low Investment	Unproven Technologies	Overall Plant Reliability
No H ₂ and Catalyst	Possible Difficult Scale-up for	Real Plant Investment &
	USP	Economics
Commercial Project was	Low Levels of HDS	Arrangement for Sale of
Initiated (Now Cancelled)	Low Levels of TIDS	Asphaltenes from ADC
ADC can Process Bitumen	Relatively Low Liquid Yield	Market Value of Sour SCO
Froth	Relatively Low Liquid Tield	Product
No Asphaltenes to		Energy Balance – Excess Energy
Thermal Cracker		/ Steam
BP Partnership for Terre		
de Grace Project		

The greatest strengths are the technical staff, the aggressive company founder, no hydrogen and catalyst requirements, and that a commercial scale project was initiated. The greatest weaknesses and unknowns are the unproven technologies, the relatively low liquid yield, and the process economics, including the value of the sour SCO product. The VCG USP Technology is a thermal process and the stability and compatibility of the product is not proven.

The long-term disposition of the bottoms product (asphaltenes, coke, unconverted VR) is a critical issue for all technologies and one that may be specific for each

project. In the Heartland Upgrader, the high sulfur (negative value) asphaltenes were to be sold as fuel. The disposition of the separated asphaltenes is a key factor in the implementation of the VCG technology.

Best Applications: Value Creation reports that the process is very flexible in terms of feedstock and product quality. However as the product quality increases, there is a significant reduction in the liquid yield (i.e., more coke and energy). The process is best suited for mild upgrading and producing a bottomless (no vacuum residue) SCO which would have an API gravity of 22-28°. The disposal of the asphaltenes is a critical factor for this application. Operation of Step 2 (USP) for SAGD feedstocks (high energy needs) should also be viable. For this application, the asphaltenes may be included in the USP feed.

Summary: Value Creation is not currently licensing the technology. It would be necessary for an interested party to participate in a project with VCG or BA Energy to utilize the technology. There was a relatively high level of technical and economic risk for the Heartland Project. The economics of the process, relative to existing technologies, is unknown. For future projects, the disposition of the asphaltenes and the revenue from the sour SCO are key factors.

VISCOSITOR

by Ellycrack A/S

Process Name: VISCOSITOR Go To: Publications Patents

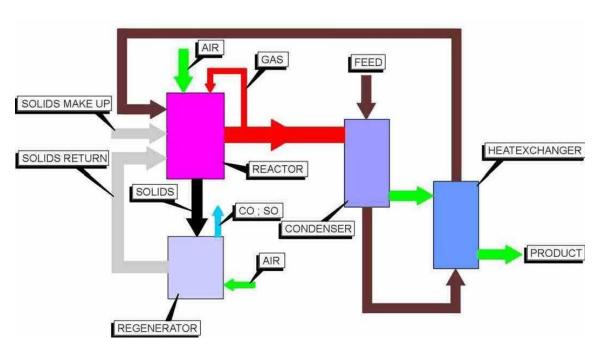
Company: Ellycrack A/S, Norway

Public Norwegian Company

Website: http://www.ellycrack.com

Process Overview & Objective: The VISCOSITOR is a non-catalytic process which thermally cracks heavy oil and bitumen and provides a fairly high level of API improvement. The process is similar to a FCC Unit in that a solid (sand) is used as a surface for coke deposition and as a source of heat. The coked sand is regenerated via combustion with air. The VISCOSITOR is also similar to the Ivanhoe Energy HTL Process but appears to be more severe. For a bitumen or Western Canadian Heavy feed, the process objective is to produce a transportable, sour SCO with 20-25 ° API gravity.

A simplistic process flow diagram for the VISCOSITOR is shown below. The heavy oil feed (brown line) is preheated in the product condenser and then further



preheated in the product heat exchanger. The feed enters the VISCOSITOR reactor along with hot solids from the regenerator and recycled hot product vapor

(thin red line). The Ellycrack patent claims that air injection to the thermal reactor is optional. The reactor is a cyclone type which is explained in the next section. Hot coked solids (sand) leave the reactor and are sent to the regenerator where they are combusted with air. Although not shown in the diagram, a portion of the regenerator combustion gas can also be recycled to the reactor to provide additional heat and cyclonic force. The vapor product from the reactor (red line) is condensed and cooled. Also not shown, are four products, condensed water, condensed hydrocarbon liquids, a product gas with light hydrocarbons, and a flue gas containing CO₂, CO, SO₂ and NO_x. This flue gas stream is sent to a CO boiler for complete combustion. SO₂ emission issues are not discussed.

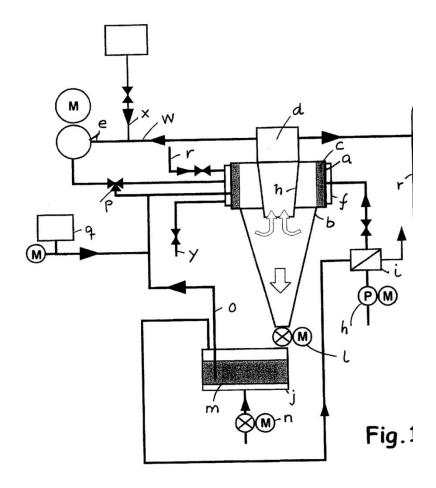
Product yields and boiling range data are not discussed by Ellycrack, however given the claimed high API gravity of the liquid product; the vacuum residue in the feed is probably nearly completely converted. The high residue conversion will result in high coke yield (large quantity of excess energy), high light gas yields and a relatively low SCO liquid yield.

Chemistry & Catalyst: According to a September 2006 press release by Wescorp Energy (former North American licensor), the VISCOSITOR technology is based in U.S. Patent 6,660,158, "Catalytic Cracking Process". This patent can be accessed by the hyperlink in *Attachment 2*. Although the patent describes a catalytic process, there is an option for using an inert material (sand) as is being specified in the current invention. This non-catalytic version of the process is being piloted and commercialized by Ellycrack.

All the patents which describe a heavy oil conversion process were invented by Olav Ellingsen of Norway. He is a highly respected and innovative scientist and remains the key technical individual for both Ellycrack. The Ellycrack heavy oil conversion technology, first named Ellycracking, and eventually the VISCOSITOR, is a result of an evolution of piloting different reactor types, designs and reactor operating conditions. The initial Ellycrack reactor design was non-catalytic and utilized mechanical stirring devices to impart kinetic energy to the heavy oil. Another design was very similar to a catalytic FCC or RFCC Unit. Although the exact evolution of the process is not precisely known, it appears that the catalytic FCC process was piloted in Norway and eventually modified to become the current non-catalytic process as described above.

In 2004, a Canadian technology investment firm, Wescorp, acquired 13% of the rights to the VISCOSITOR Process. The process was then valued at \$5 MM. The agreement was modified to include 25% ownership and to establish a 50/50 joint venture for the process licensing rights in North American. Initially (2004-2006), Wescorp had been actively marketing the process (press releases – but with no publications) and planned to build a large (200 BPD) pilot/demonstration plant in Canada. Although the pilot plant design was completed by Bantrel, it was decided in 2006 that it was more effective to move the 50 BPD VISCOSITOR from Norway to Canada and build the larger unit after final process optimization was completed. This clearly indicates that it was premature to invest in such a large unit and that the VISCOSITOR is a developing process with recent critical modifications which have been employed to meet API gravity improvement objectives. Wescorp and Ellycrack have since (September 2009) restructured the agreement so that Ellycrack has full ownership control and Wescorp simply owns 23.7% of the Ellycrack AS stock.

The VISCOSITOR Reactor as depicted in the key patent is shown below. The feed enters via pump h. The feed preheat scheme shown in the patent is different than shown in the previous figure (from Ellycrack website). The feed enters the cyclonic reactor via plenum f where it is combined with hot recycle product vapor



(stream r). The combined feed and recycle vapor is introduced tangentially into the cyclone. To have the velocity required, the rate of recycle stream r must be fairly large. The feed oil reacts in the "bed" of hot sand which is also introduced tangentially and is forced on the inner walls of the cyclone. The heavy sand will drop via gravity to a rotating valve and into the regenerator. The reactor products (vapor state) leave via the inner duct and flow out at point d. The regenerated

sand is pneumatically transported to the cyclone reactor using product vapor at

point p. Make-up sand enters from bin q. Purging of spent sand (required) is not

indicated.

The major Ellycrack and Wescorp claims are high API improvement and low

naphtha olefin content. No other product quality data are provided. Very

importantly, liquid yield is not discussed. Spent sand disposal and flue gas

treatment are not addressed. Long-term representative pilot tests are required to

adequately assess the real sand make-up rate. The absence of the above items

points towards a developing technology.

Product & Waste Issues: As with any thermal process, there are issues with the

stability of the liquid product. The liquid product should be similar to a delayed

coker product, although 1) the residence time in the VISCOSITOR is short, and 2)

the vacuum residue content should be low as indicated by the high product API

gravity. Both these factors should decrease instability, however complete testing,

including compatibility with other liquids, would be required to determine if the

product is stable. A Wescorp press release claims that the product has low olefin

content and maintained stability in storage after a few months. This is

encouraging but not convincing of the product stability.

Another product issue is the venting of the waste gas containing SO₂ and NO_x.

This will require either that the CO boiler is a fluidized-bed type or that the gas is

scrubbed before venting to the atmosphere. The disposal of the metals laden sand

will also present a disposal issue.

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Scale-up: The VISCOSITOR pilot plant currently located in Canada is 50 BPD. This is fairly large unit and will make subsequent scale-up easier. The size of the physical reactor is not known. The original pilot plant plans were to build a 200 BPD unit, indicating that they believed that additional scale-up is required. The VISCOSITOR reactor is difficult to scale-up due to the cyclonic reactor and assurance of correct tangential and linear velocities. For other areas of the process, Ellycrack can rely on the FCC process scale-up experience.

Patents: Ellycrack S/A has issued several patents on heavy oil upgrading, all with Mr. Ellingsen as the inventor. The current key patent is U.S. 6,660,158 which was quoted by Wescorp (former North American licensor) as the basis for the current process. A 2007 U.S. patent application appears to be similar to the base patent. The patents contain primarily background information and complicated drawings and a process description. No heavy oil upgrading data are provided. The Ellycrack website states that additional patents are being filed on the optimized process; this may have included the patent application mentioned above.

R&D Facilities: Prior to 2007, R&D was conducted at the Trondheim, Norway facility. At least a 50 BPD unit and possibly other smaller units were available. The exact process components included in the pilot plant (i.e., regenerator) are unknown. The length of a typical test is also not known but a long-term test is required to insure a clean, equilibrium operation in a commercial unit. In September 2006, the 20-50 BPD pilot plant was shipped to Winnipeg where it is was upgraded. The unit was moved in October 2007 to the Saskatchewan Research Council in Saskatoon where it slowly undergoing additional modifications. A start-up data has not been announced as of late 2009.

Current Status: Wescorp had been active in the 2004-2006 timeframe but since 2007 has not been actively marketing the technology. Similarly, Ellycrack AS is not active in the promotion of their technology. Some highlights from the website and other sources are itemized below:

- 1. Modified Agreement with Wescorp In September 2009, Wescorp and Ellycrack restructured their 2004 agreement so that Ellycrack AS has full ownership control (including the pilot unit at the Saskatchewan Research Council) and Wescorp simply owns 23.7% of the Ellycrack AS stock. Wescorp is no longer marketing the Ellycrack (VISCOSITOR) technology and it is not mentioned on their website.
- 2. Norsk Hydro Ellycrack had previously operated their Norwegian pilot plant for Norsk Hydro. A feedstock API gravity increase, using single-pass operation, of 18° to 28° was reported. Norsk Hydro has requested additional technology details including a material and energy balance. The product was reported to be initially stable (i.e., low olefins) and also stable after months in storage.
- 3. Pilot Plant Designed / Moved In early 2006, Bantrel completed the engineering phase for a 200 BPD VISCOSITOR to be located in Canada. This was part of the agreement between Ellycrack and Wescorp Energy. By mid-2006, however, it was decided not to build the large pilot/demo plant but to instead move the 20-50 BPD pilot unit from Norway to Canada. The unit was transported in September 2006, modified and upgraded in Winnipeg and moved to its final location (Saskatoon) in October 2007. Since then, efforts to commission and start-up the unit have been delayed and of late 2009, there is no status update from Wescorp or Ellycrack.
- 4. <u>Pilot Work in Norway</u> In late 2005, the Norway pilot plant evaluated the processing of three important heavy oils, including Lloydminster crude. It is not certain if the Ellycrack process configuration used for these tests is the same as that marketed today (i.e., the VISCOSITOR).

The press release mentioned "mechanical upgrading" and no "special catalyst". A summary of the available test results is shown in the table and indicates a minimum of a 10° API gravity increase and the

production of a transportable SCO. No yield data were provided.

Crude	Feed API, °	Product API, °
Venezuela _PDVSA	9.3	20.0
North Sea – Grane	18	29.5
Lloydminster	13.2	25.2

5. Ownership and Joint Venture with Wescorp Energy – In 2004, Wescorp acquired a 13% of the rights to the process. The process was then valued at \$5 MM. The agreement was modified to include 25% ownership and the creation of a 50/50 joint venture for process licensing in North America.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the VISCOSITOR is shown below.

<u>Strengths</u>	<u>Weaknesses</u>	<u>Unknowns</u>
Innovative Design	Newcomer to Upgrading	Amount of Excess Energy
Good Patents	Process Complexity	Product Stability and Compatibility
Pilot Plant Data Obtained	Limited Published Data	Actual Liquid Yield
Relatively Large Pilot Plant	Scale-Up May be Difficult	Sand Make-up Rate
High API Gravity, Transportable SCO	Required Flue Gas Treatment	Recycle Required to Make Transportable SCO
No Catalyst / Hydrogen	Estimated Low Liquid Yield	Investment Cost & Economics
No Net Coke Product	Spent Sand Disposal	
Fits with SAGD Project	High Operating Cost	
	Still Being Optimized	

From a technical standpoint, the greatest strengths are the ability to produce a high API gravity product without catalyst and hydrogen, and the relatively large pilot plant awaiting start-up in Canada. The greatest weaknesses are the process complexity, the estimated low liquid yield, and the continuing optimization (major design modifications). Major unknowns are the product stability, amount of excess energy and the required investment cost. The current lapse in marketing efforts and start-up of the pilot plant in Saskatoon is disconcerting.

Best Applications: The VISCOSITOR is best suited for field applications for producing a partially upgraded SCO. The process appears to produce a large quantity of steam (although not discussed by licensors) and is thus suitable for a SAGD application. The claim of a pumpable 20-25°API gravity product is actually more severe than required to meet the minimal specification for a transportable SCO and may result in a higher product valuation.

Summary: Based on published data, the VISCOSITOR appears to be a good process for a SAGD operation since it produces a transportable, sour SCO and does not require catalyst or hydrogen. A high API gravity improvement is claimed, which is only also possible with a low yield of liquid product and a great deal of excess energy.

There are no or limited data for key process information such as the liquid yield, waste sand quality and rate, excess energy, product stability and estimated investment. In this regard, the VISCOSITOR lags the Ivanhoe HTL Process in terms of development/commercialization status. An advantage of the VISCOSITOR is the high liquid product API and the near elimination of the feedstock vacuum residue. The process will require additional years to fully develop. The technology is interesting and has some potential for commercialization. When the Canadian pilot plant is operational, the technology can be completely investigated.

Wildcatter HCU Process by Refinery Science

Process Name: Wildcatter Hydrocracking Unit Go To: Publications Patents

Company: Refinery Science Inc., Vancouver, BC

Canadian Public Company – Limited Ownership

Website: http://www.refineryscience.com/

Process Overview & Objective: The Wildcatter HCU Technology is an incompletely developed, heavy oil conversion/upgrading process, developed by Refinery Science Inc. (RESI). The process is modular in design and includes catalytic thermal cracking, carbothermic reduction, and Fischer Tropsch (FT) to produce a high yield of sour SCO product with no solid coke yield. There is no secondary hydrotreating and thus no hydrogen requirement. On the surface, the technology will meet the needs for partial upgrading in Western Canada. The process is targeting SAGD applications and is specifying small (1,000–2,000 BPSD) Wildcatter modules for field application.

The process has four primary steps: 1) "catalytic" / thermal cracking of the heavy crude feed using a molten liquid heat carrier, 2) carbothermic reduction of the product coke from Step 1 to produce CO and H₂, 3) catalyst recycle, and 4) Fischer Tropsch conversion of the syngas (CO and H₂) to liquids. RESI's primary development work has been related to Step 1. The last three steps all relate to the disposal or processing of the solid coke using existing technologies. RESI is collaborating with two separate firms regarding the small-scale development of the carbothermic reduction and FT steps.

The first process step is the primary focus of the RESI efforts and is piloted at their El Paso R&D site. The "catalytic" thermal cracking process developed by RESI is novel and significantly different from traditional technology.

Claims: The critical RESI claims relative to the Wildcatter HCU are:

- 1. High liquid yield (> 100%)
- 2. Low pressure operation in Step 1
- 3. No net coke product
- 4. Modular (1,000–2,000 BPD) design
- 5. Operating cost of less than \$2/Bbl
- 6. Can produce the required steam for SAGD application
- 7. Estimated capital cost of \$10,000/BPSD of installed capacity
- 8. Ability to make an approximate 25°API gravity, medium sulfur SCO from Athabasca bitumen
- 9. Small footprint plant with low greenhouse gas emissions

Many of these claims are based on initial pilot work and preliminary engineering studies and will definitely evolve as the process is further developed.

Product & Waste Issues: The liquid from a thermal cracking process, even if catalytic as for the Wildcatter Process, may be unstable. This is particularly true for the light ends which can contain diolefins and olefins. The Wildcatter Process will produce a SCO which is a blend of thermal cracked and Fischer Tropsch liquids. Compatibility of this final SCO is therefore a concern.

Scale-up: Since RESI is planning on small modules for their process, scale-up may not be a large concern. The Step 1 pilot plant (15 BPD) however, is still a large step from the 1,000 BPD commercial module. The Wildcatter carbothermic reduction and FT modules may require a 'scale-down" from the equipment currently utilized in the commercial scale. At this stage in the process development, scale-up is not a critical issue for RESI.

Patents: Refinery Science (D. Redina and E. Hauptmann) issued a U.S. patent application in September 2008. The application describes the overall process but does not provide any data or examples. This is the only patent application relative to the Wildcatter HCU Process. In their IPO prospectus, RESI list several patents that they have licensed from universities and sister companies. In 2007, one of the principals of RESI, who is a professor at the University of Texas, was granted a patent related to the use of molybdenum sulfide as a cracking catalyst for heavy oils. Most of the listed patents are more specific to materials selection and to particular catalysts.

R&D Facilities: The RESI pilot plant is a demonstration of the first step of the Wildcatter Process. The unit can process 15 BPD of heavy crude and appears to contain all the equipment envisioned for a commercial unit.

Current Status: Listed below are some of the important items concerning the Wildcatter HCU and RESI. By far, the highest level of activity is the operation of the pilot plant and the efforts to raise \$30 MM for a demonstration facility.

- 1. Public Sale RESI attempted to raise \$30 MM to advance their technology though a public offering. In June 200, RESI issued a SB-2 with the U.S. SEC. The \$30 MM would have been used to lease oil reserves and to construct a 1,000–3,000 Wildcatter HCU. The status of the public offering is not clear but appears to have been withdrawn in January 2009.
- 2. <u>Pilot Facility</u> The 15 BPD pilot plant was started-up in early 2007 and has operated successfully on various feedstocks and catalysts.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the Wildcatter HCU is shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Unique Technology	Complexity and Integration of	Market Valuation of
High Liquid Yield	Process Steps Process not Completely Developed Product Compatibility and	SCO Effect of Small Modular
Tingii Liquid Tield		Design on Profitability Final Total Investment
Operating Pilot Plant	Stability Concerns	Cost
Strong Scientific Staff	Small-Scale Carbothermic Reduction&Fischer Tropsch Plants	Scale-Up Issues
No Hydrogen Requirements	Engineering Capability	
No Net Coke Product	Expensive and Complex Catalyst Recycle	
Fits with SAGD Projects		

The greatest strengths are the high liquid yield, no hydrogen or coke product and the fit with SAGD. The process is a very unique technology with no similar analog in the refining industry. The greatest weaknesses are the process complexity, envisioned scale of operation, and that the process is not completely developed or optimized. The final process plant investment, operating cost and profitability are large unknowns at this point in the technology development.

Best Applications: Given the quality of the SCO, modular design and excess energy created from the process, the Wildcatter technology is most applicable to SAGD operations. This is consistent with the RESI target which is field application for SAGD projects in Western Canada.

Summary: The RESI Wildcatter Technology is a unique technology targeting partial upgrading in the field and the production of a high yield of approximately 25°API SCO. Although this fits well with typical field upgrading processing objectives, the Wildcatter process is in its early stages of development and it will be several years before the technology could be ready for commercialization.

WRITE Process by Western Research Institute

Process Name: WRITE Process Go To: Publications Patents

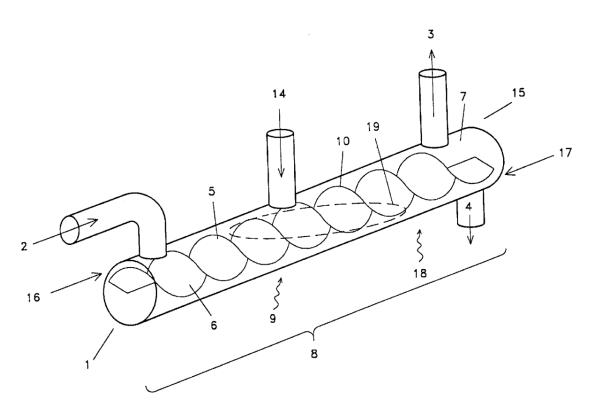
Company: Western Research Institute, Laramie, WY

Website: http://www.westernresearch.org

Process Overview & Objective: The WRITE Process is a new, incompletely developed, partial upgrading process, developed by the Western Research Institute (WRI), a private not-for profit organization, primarily funded by the U.S. DOE. WRITE denotes Western Research Institute Thermal Enhancement. The process was developed using basic concepts from another government-funded process developed by WRI, the TaBoRR (Tank Bottoms Recovery and Remediation) Process. Work on the WRITE Process began in 2002 and the process concept was announced in 2004/2005. The SCO product will not contain vacuum residue, however the process is still considered partial upgrading since the sour SCO product will just meet pipeline specifications and WRI is targeting field application at SAGD sites.

The process is fairly simple in concept and employs an atmospheric distillation of the heavy oil or bitumen followed by continuous coking of the resulting atmospheric residue. The coker and straight run liquids are combined to form the sour, but bottomless SCO. Initial pressurization of the bitumen feedstock following by a flash to remove water, is also discussed. The coker-derived naphtha contains significant diolefins and olefins and must be either excluded from the SCO or hydrotreated. Disposal of the coke product is not emphasized by WRI but will require fluidized-bed combustion (limestone for sulfur absorption) and will be a major cost component of a WRITE commercial plant. The process is targeting field location and SAGD applications.

The process has two major steps: 1) atmospheric stripping or distillation (named a DRU – Distillate Recovery Unit) and 2) processing of the atmospheric or stripper bottoms in a continuous coking device. As mentioned above, the overhead from the DRU plus the condensed coker liquids are combined to form the SCO product. The coker naphtha, which is approximately 6 W% of the SCO, may be separated and hydrotreated or presumably used as fuel. The key technology feature is the continuous coker which is a currently a rotary screw device, although WRI also mentions that other devices can be utilized. A sketch of the continuous coker is depicted below which was taken from one of the WRI patents. The device is



typically pitched downward to assist in the movement of the liquid feedstock and removal of the coke. The heavy feedstock (atmosphere residue or stripper bottoms) enters at point 2 in the figure and is moved via the screw device. Heat is externally applied (shown as 9) and heats the liquid to a coking temperature. Volatilized feedstock and gaseous conversion products exit at nozzle 3. The liquids are recovered via downstream cooling. The coke product exits at nozzle 4.

Sweep gas, which aids in the stripping of the conversion products from the device,

enters at nozzle 14. To apply the required heat, the device can be located in a

fluidized bed of hot sand. Sealing of a device having a rotating mechanical

apparatus are of high concern.

Claims: The critical WRI claims for the WRITE Process are relative to continuous

coking and the stability/compatibility of the blended SCO product. WRI claims

that a continuous coker has a lower capacity threshold than commercial semi-

batch coker and, based on laboratory analyses of the WRITE liquids, will produce

a more stable/compatible product.

A 60-80 W% net liquid yield, including naphtha, is claimed with all pipeline

specifications being met. It is not clear, however it appears that the naphtha in the

SCO (all coker derived) is recovered, hydrotreated to reduce diolefins/olefins and

reblended into the SCO. Coke is reported as 75 Lb/Bbl or approximately 21 W%

of total feed; this is a fairly typical value.

Product & Waste Issues: The liquid from a thermal cracking process, even if

claimed to be better quality than delayed coker liquids, may be unstable. This is

particularly true for the light ends which will contain diolefins and olefins. WRI

has conducted stability and compatibility testing and claims that the product is

acceptable. The applicability of the tests utilized by WRI and whether the naphtha

was included in the liquid tested is unclear. Stability and compatibility of this final

SCO is a concern.

Coke and acid gas disposal are also an issue. The coke can be sold or burned in a

FBC to produce the steam for the SAGD process. The burning of the high sulfur

coke will necessitate the use of limestone absorbent which could result in a

significant disposal issue at a field facility.

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Scale-up: The capacity of a commercial scale WRITE Unit is unclear. From the

WRI patents, it is estimated that a single screw coker could process in the range of

1,000-2,000 BPD of bitumen feedstock. A 20,000 BPSD WRITE commercial

plant would then require 10–20 coker units. Scale-up of the mechanical rotary

screw coker will be an important issue and is a large concern. At this stage in the

process development, scale-up is not a critical issue for WRI.

Patents: Two U.S. patents relating to the WRITE Process have been issued to

WRI. These similar patents are very lengthy, difficult to read, and have numerous,

similar claims. They appear to describe many versions of the process, including

the one discussed in this summary. WRI also issued a U.S. patent application in

September 2008 which discusses numerous methods of staged thermal processing

of heavy feedstocks. This application may not be directly applicable to the current

process configuration but have an impact on future WRITE Process

configurations.

R&D Facilities: The WRITE Process pilot plant is located at WRI's Advanced

Technology Center in Laramie, WY. The pilot plant appears to process 1 BPD

and contains the DRU and a 6-inch rotary screw coker. A larger PDU has been

discussed to investigate scale-up and other issues not adequately addressed in the

pilot unit.

Current Status: Since the publication of papers and filing of patents in the 2004

to 2005 timeframe, the level of activity relative to the WRITE Process appears to

be low. This may be a consequence of the current (mid 2010) limited U.S.

attention and funding for fossil fuel research.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the WRITE Process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
U.S. DOE Supported	Complex Mechanical	Market Valuation of Coker
	Coking Device	Derived SCO
Data on Cold Lake &	Process not Completely	Downstream Recovery Issues
Athabasca Bitumen	Developed	Related to Coker Liquids
Operating Pilot Plant	Product Compatibility and	Final Total Investment Cost
	Stability Concerns	Thiai Total investment Cost
Strong Scientific Staff	Low Liquid Yield	Scale-up of Coking Device
Can Fit with SAGD Project	Coke Product will Require	
	Expensive FBC	
Low Pressure	Naphtha may Need to be	
	Excluded from SCO	

The greatest strengths are the low pressure design, DOE financial support, operating pilot plant, and the fit with SAGD. The greatest weaknesses are the envisioned maintenance and scale-up issues associated with the rotary screw coker, the low liquid yield, the SCO product stability and that the process is not completely developed. The final process plant investment, operating cost and profitability are large unknowns at this point in the WRITE Process technology development.

Best Applications: Given the quality of the SCO, modular design and excess energy (coke and light gas combustion) created from the process, the WRITE Process is most applicable to SAGD projects.

Summary: The WRITE Process is targeting field partial upgrading and the production of a sour bottomless SCO comprised of straight run and coker liquids. Although this fits well with typical field upgrading processing objectives, the

WRITE Process is in its early stages of development and has several technical hurdles to overcome before advancing to the next stage (demonstration unit) of development.

Full Upgrading Processes

Chattanooga Process

by Chattanooga Corp.

Go To: Publications Patents

Process Name: Chattanooga Process

Process Type: Fluidized Bed Hydrogen Addition Company: Chattanooga Corp., Somerset, NJ

Private U.S. Company

Website: http://www.chattanoogaprocess.com

Process Overview & Objective: The Chattanooga Process is a fluidized-bed hydrocracking technology which processes the oil sands from a bitumen mine site and produces spent sand, a bottomless (no vacuum residue) SCO and gases. The process is unique in that the raw tar sands, not the extracted bitumen, are the feedstock to the process. This alleviates the need for extraction and froth treatment plants and eliminates the tailings pond. The heart of the process is the Chattanooga fluidized-bed reactor which provides a combination of thermal cracking and hydrogenation. The fluidized-bed reactor operates at high temperature (800-1000°F) and moderate pressure (600 psi) and is fluidized with very hot (1500°F) hydrogen. The hydrogen rate is 15-26 times that required for chemical consumption; for ebullated-bed processing it is about 3 times. Catalyst (type not specified) can optionally be added with the tar sands feedstock. The process is claimed to produce a fairly high yield of bottomless (no vacuum residue) SCO which will have an API gravity of 25-30° and will meet Canadian The process was originally developed for oil shale pipeline specifications. upgrading which contains very little vacuum residue.

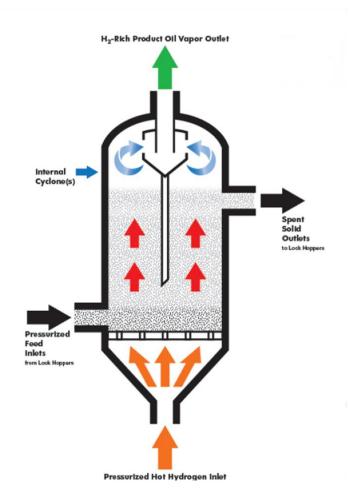
Chattanooga states that the process can also process bitumen from SAGD operations and result in an overall energy balanced operation. The fluidizing medium for the SAGD operation would be "imported" sand.

Chattanooga Corp. was formed in late 1990's with the objective of commercializing the process for both shale oil and tar sands upgrading. Patent applications were filed beginning in 1997. The company personnel are comprised

of several retired industry experts and experienced managers. Chattanooga Corp. does not appear to have a full time staff and a dedicated business location. With no revenues, the funding for Chattanooga's activities (patents, commercial estimates R&D), is probably from private sources and government grants.

A sketch of the Chattanooga Reactor is shown below. The solids fluidized are the tar sands which enter the bottom of the reactor via multiple feed injection points.

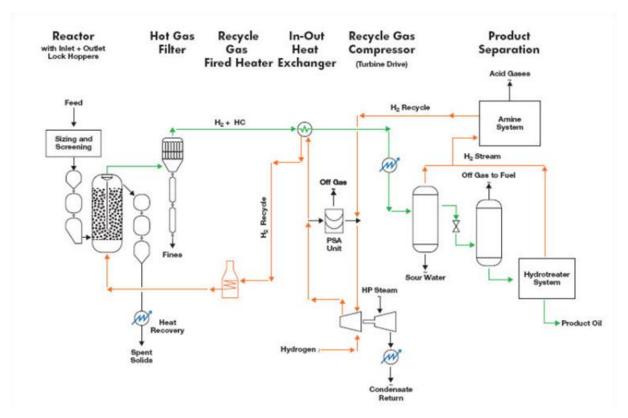
The tar sands are pressurized in multiple lockhoppers using hydrogen. The reactor fluidized by hot $(1500^{\circ}F)$ hydrogen which is a combination of make-up and recycled material. Recent patent applications discuss the inclusion light hydrocarbon (methane and ethane) in the fluidization gas. The sand residence time in the reactor is approximately 15 minutes. This sufficient to attain complete hydrocracking of the bitumen residue with some accompanying hydrogenation



due to the hydrogen partial pressure in the reactor. Spent solids, which contain some coke (1-1.5 W%), are removed at the top of the reactor. These solids are depressurized via lockhoppers and cooled in an air/solids exchanger and eventually sent to landfill. The vapor product, containing the non-condensable

hydrocarbon gases, acid gases, volatilized conversion products, and unreacted hydrogen exits the reactor via primary cyclones. Downstream of the reactor, additional secondary cyclones and an electrostatic precipitator or Pall filter are utilized to completely remove the solids from the gaseous reactor effluent.

An overall process flow diagram for the Chattanooga Process is shown below. The



flowsheet is fairly representative of a typical hydroconversion process flowsheet with the exception of the solids treatment steps including the spent solids heat recovery.

Claims: The important Chattanooga Process claims include the use of a unique fluidized-bed reactor which can be fed the oil sands directly and can produce a reactor effluent with little or no vacuum residue and a spent product which can be landfilled. The reactor operating conditions for a tar sands application appear to at

approximately 900°F and 600 psig. The energy required to heat the oil sands and the heat of reaction is provided by the feed hydrogen. Since thermal cracking is endothermic but hydrogenation is exothermic, the heat of reaction could be small. The hydrogen is fed at a very high rate (15-26 times the chemical consumption) and at a temperature of 1500°F. The determination of the hydrogen feedrate to the reactor has dual constraints: to satisfy the energy balance and to provide the required fluidization velocity in the reactor. In practice, the rate of hydrogen is set to obtain the required bed level in the reactor and the temperature from the fired heater (i.e. firing rate) is varied to control the reactor temperature.

The Chattanooga patents indicate a wide range of SCO yields from an Athabasca tar sands feed. A published set of expected yields and product qualities is not available. The patent value of approximately 77 V% on bitumen fed would be indicative of a process with a high coke yield. This is not consistent with a hydrogen consumption of 2.8 W% (1,850 SCF/Bbl) as reported in the patent. At this time it is not possible to completely assess the Chattanooga Process performance until consistent set of actual laboratory or expected commercial yields and product qualities are published.

The optional use of a catalyst, which is included in the oil sands feed, is not clear. Without catalyst, the Chattanooga Process SCO would have an API gravity of 27-32°, with catalyst injection, the SCO API gravity would be in the 34-35° range. If the catalyst is required, a cost of \$2-3/Bbl of bitumen feed could be incurred based on the Chattanooga patent. Additionally, the spent catalyst would be included in the spent sand from the facility and may present issues relative to direct landfilling.

Other Chattanooga Process claims involve the cooling of the spent sands, type of

feedstock to the hydrogen plant, preheating of the fired heater air, etc. These are

not critical at this phase of the process development. These items may have a

large impact on the process efficiency and investment cost but not on the technical

feasibility of the process concept.

Product & Waste Issues: The Chattanooga Process produces a great deal of spent

sand product which will contain coke. The type of contaminants on the spent sand

has not been published although Chattanooga states that the spent sand can be

utilized for land reclamation. A coke yield of approximately 13 W% of feed,

resulting in 1-1.5 W% coke on the spent sands, has been reported. Approximately

1.5 tons of sand is produced for each barrel of Chattanooga SCO.

Implementation of the process will require typical Upgrader waste treatment plants

including water treatment, sulfur recovery and amine treating. Since the

Chattanooga Process attains near 100% residue conversion, the SCO product

should be stable from the standpoint of asphaltene precipitation. Given the

relatively low hydrogen partial pressure, the conversion naphtha may contain

unstable material (olefins and diolefins) and would require hydrotreatment before

transportation in a pipeline.

Scale-up: The process was piloted in a relatively small (5-10 gal/day SCO) NCUT

pilot unit. It is not known if the pilot unit included many of the solids handling

operations expected in a commercial Chattanooga Plant. The process will require

significant large-scale piloting to address some large scale-up issues. This is

recognized by Chattanooga since a 100-400 BPD demonstration plant is planned.

Many of the scale-up issues involve the reactor design and ensuring proper fluidization and a heat balance. This scale-up may result in relatively small feedstock capacities for a maximum size reactor or may result in the specification of additional energy input to achieve a commercial heat balance. Other important scale-up issues are related to the handling of the solids. This would include the extremely large feed and product lockhoppers required for a commercial tar sands feedrate, internal cyclones in a hot high pressure vessel, the design of the very large spent sands coolers, and the specification of an electrostatic or other tertiary separator (e.g. Pall-type filter) for a high vapor rate.

Patents: Three U.S. patents were issued to Chattanooga Corp. in 1999, 2000, and 2001. A fourth patent was assigned to C. Kirkbride (Chattanooga founder) in 1997 and described an early version of the process concept. The latest two patents (issued in 2000 and 2001) appear to describe the current reactor and process fairly well. Operation at 800-850°F is described in one patent and 900-1000°F in the second. These patents are well written and comprehensive. Claims include downstream heat integration and cooling of the spent sand.

There are also three U.S. patent applications, one filed in 2002 and two in 2005. The 2002 appears to a continuation of the patents granted in 2000. The two applications filed in 2005 add new embodiments to the prior patents including the inclusion of light hydrocarbon gases in the vapor feed stream, feeding of bitumen to the reactor in addition to the tar sands, and the processing of SAGD bitumen in the Chattanooga Reactor using "imported" spent sand.

R&D Facilities: The Chattanooga Process has been piloted using two experimental units at the NCUT laboratory in Edmonton, Alberta. The first pilot plant was commissioned in 2000, the second in 2004. The initial NCUT unit was

a continuous stirred reactor (~100 cc/hr feedrate). The latest pilot unit is a 4-inch diameter by 20-inch bed height fluidized-bed reactor system which processes 4-8 kg/hr of shale. In oil sands operations, this capacity is estimated to be equivalent to a 5-10 gal/day SCO production rate. Much of the pilot work appears to be on oil shale feedstocks. The oil sands or bitumen feedstocks tested and number/duration of tests is unavailable.

Current Status: In the period 2004-2008, Chattanooga Corp. had a fairly high level of activity in the preparation of patent applications, experimental studies at NCUT, and several presentations at technical conferences (See Attachment 1). The next announced step is obtaining funding for a demonstration plant, although no schedule, cost estimates or partnering activities have been publicized. There has been no news from Chattanooga in the past two years.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the Chattanooga Process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
Unique Reactor Concept	Process Complexity	Spent Sands Coke/Oil Content
Patents Granted	Low Liquid Yield for Hydrogen Addition Process	Scale of Pilot Plant
NCUT Pilot Plant Data	Low Feed Capacity per Reactor	Process Economics
Eliminates Extraction and	Scale-up of Solids Handling	Data with/Without Optional
Froth Treatment Plants	Equipment	Catalyst
High Quality SCO Produced	High H2 Recycle Rate – High Operating Cost	Catalyst Type and Cost
Quality of Technical Staff -	Many Years from	
Engineers not Scientists	Commercialization	
Moderate Pressure		

The greatest strengths are the unique concept which eliminates the extraction and froth treatment facilities, and the capability to produce a SCO meeting Canadian pipeline specifications. The greatest weaknesses are the reported (from patents) low liquid yield, process complexity (solids handling and very high hydrogen recycle rate), and expected difficult process scale-up. The process is in the initial development stage and is many years from possible commercialization. The Chattanooga Process will require a high plant investment and a high operating cost, however with the elimination of the extraction and froth treatment plants it may be economically attractive.

Best Applications: With the feedstock to the Chattanooga Process being mined tar sands, the preferred application is clearly a mineable bitumen project. Without secondary hydrotreatment, the process can produce a 25-20° API SCO, with hydrotreatment and possible hydrocracking, a +30°API SCO is produced. Although Chattanooga claims that the process can be applied to a SAGD bitumen and result in an energy balanced project, it would require the importing of a large quantity of sand as a fluidizing medium and as an outlet for coke and contaminant metals. It does not appear that SAGD bitumen is practical application for the Chattanooga Process.

Summary: The Chattanooga Process is a unique fluidized-bed, full upgrading process for which the feedstock is the solid tar sands. The process is in the initial development phase and is many years from possible commercialization. There are significant technical issues primarily related to solids handling and scale-up concerns. The production of a bottomless SCO from Athabasca bitumen feedstock is claimed based on small-scale pilot work. If the process can be proven at the demonstration plant scale, it may be economically feasible due to the elimination of the extraction and froth treatment plants and the tailings pond.

Genoil Process

By Genoil

Go To: Publications Patents

Process Name: Genoil Process

Process Type: Fixed-Bed Hydrogen Addition

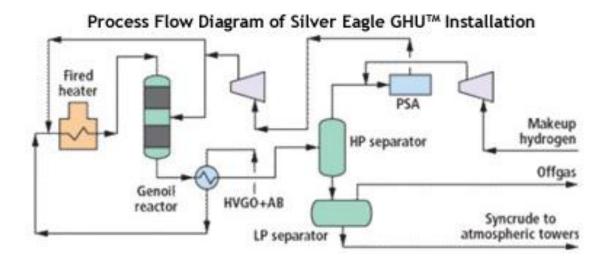
Company: Genoil, Alberta

Public Canadian Company

Website: http:/www.genoil.ca

Process Overview & Objective: The GHU Process is a fixed-bed catalytic hydrocracking technology not significantly different from those licensed by Axens, Chevron, Shell and UOP but with a single new feature. As such it is a full upgrading process with no vacuum residue in the SCO product. This new feature incorporates premixing of the hydrogen with the feed oil using a proprietary mixing device and at operating conditions which result in good hydrogen dispersion in the oil. According to Genoil and their Canadian patent, this results in less severe operating conditions in the GHU hydrogenation reactors (lower hydrogen partial pressure) and reduced overall plant investment. The current major Genoil claims are high HDS, CCR and residue conversions for heavy crudes including Athabasca bitumen. Genoil Inc. originated in 1998 and was formerly known as CE3 Technologies.

A process flow diagram for the GHU Process as applied at the first planned (now cancelled) commercial installation in Utah is shown on the following page. A single reactor is shown, although multiple reactors are typically required. With the exception that a portion of the hydrogen feed is fed upstream of the fired heater, it is identical to a typical hydroconversion process flowsheet.



Claims: The unique chemistry announced by Genoil involves the premixing of a portion of the feed hydrogen with the vacuum gas oil or residue feedstock prior to entering the GHU Reactor. In mid 2009, Genoil has claimed other unspecified enhancements. The injection of hydrogen utilizes a proprietary mixing device which saturates the liquid hydrocarbon with hydrogen above normal equilibrium saturation levels. According to the Genoil patent, the key aspect of the process is to preheat and disperse the hydrogen at near molecular level into the liquid hydrocarbon stream. Intimate dispersion of hydrogen is thus attained (claimed).

The major claim is that the high level of hydrogen dispersion results in improved hydrogenation and cracking reactions in the GHU fixed-bed reactors such that the reactor operating conditions (temperature, hydrogen partial pressure) can be reduced relative to existing commercial processes. The GHU is a multi-stage reactor system and the Genoil patent application and planned Utah installation included vapor/liquid separation between at least one of the reactor stages.

Consistent with the lower required hydrogen partial pressure, Genoil claims lower hydrogen feed/recycle rates resulting in reduced operating costs. A typical fixed-

bed hydrocracker will feed 3 to 5 times the hydrogen consumed in the process; the Genoil patent claims just 1.15 - 1.30 times the hydrogen consumption. Since the reactor kinetics and degree of product stability is determined by the reactor hydrogen partial pressure (i.e. not the hydrogen rate), this Genoil claim is not significant. For example, to attain a specified hydrogen outlet partial pressure, which is the parameter required for kinetics and product stability, a reactor could be designed at high total pressure with a low hydrogen feedrate or conversely, it could be designed at a lower total pressure but utilizing a higher hydrogen feedrate. It is the combination of total pressure and hydrogen treat gas rate which determines the reactor hydrogen outlet pressure. Overall upgrader economics will dictate the best combination of total pressure and gas rate for the required outlet partial pressure. Based on Consultant's studies and borne out by commercial design and operation, a ratio of hydrogen fed to that consumed of approximately 3 -5 provides the best overall economic return.

Genoil does not provide any data with and without the premixing of hydrogen which could directly support their major claim. Given the over 50 years of hydrotreating / hydrocracking industry R&D, it would be surprising that this premixing concept was not previously evaluated. However, the possibility exists that the Genoil innovation could be a valuable enhancement to heavy oil processing. If true, the comparative data discussed above should be highly touted in the Genoil patent applications and company publications. The lack of this supporting data increases skepticism concerning the Genoil Process claims.

Genoil has specified typical fixed-bed catalysts such as those manufactured by Criterion and Akzo Nobel. The unit designed for the Utah application utilized four fixed-bed reactors for a heavy vacuum gas oil feed (atmospheric bottoms is also mentioned as a feedstock). With the low unit feedrate (1,200 BPSD), it is

certain that these four reactors are arranged in series and contain different catalysts for handling metals removal, cracking and HDS. As with all fixed-bed processes operating on high metals bitumen, one or more guard beds with a demetalization catalyst are typically specified to increase the overall catalyst cycle time.

Genoil has published yield and process performance data on Athabasca bitumen feedstock (whole crude) claiming high conversion (80%) and high HDS (95%). These results were obtained at low total pressure and reactor temperature and using standard catalyst. These fixed-bed reactor results are only possible at the start-of-run (SOR) conditions. Rapid deactivation due to catalyst pore mouth plugging by coke and contaminant metals, particularity in the initial beds, would allow operation for only a few weeks. Catalyst life would be very short. Recently, Genoil is more realistically stating that a multi-reactor system with swing-type guard beds and two or more HDS/HDN reactors are required to process Athabasca bitumen. Given the high feedstock metals content, high conversion fixed-bed processing is borderline technically attainable and is not economically feasible.

If the mixing device is beneficial for lower design pressure, the target application of the GHU should be the current fixed-bed applications, not extending the well-established operating envelope by touting short-term pilot results.

Product & Waste Issues: For moderate conversion operation (<55%) on atmospheric and vacuum residue, there should be no issues with GHU products. For higher conversion operation, particularly with the relatively low hydrogen partial pressure claimed, there are large concerns with the stability and compatibility of the GHU unconverted residue. Besides a great deal of spent catalyst (guard beds) when processing high metals bitumen, there should not be

any waste issues with this process.

Scale-up: The scale-up from the Genoil 10 BPD pilot plant to a demonstration

facility was planned for the Utah facility; however the project was cancelled due

to the sale of the Siler Eagle refinery. If an initial scale-up to a demo scale is

successful, then the additional scale-up from the demonstration facility to a

commercial size (25,000 BPSD) should not be difficult. Genoil is not a large,

mature hydrogenation technology company and there will be a learning curve

involved in the scale-up, particularly from the pilot to a demonstration unit. Many

of the scale-up issues involve the reactor design and ensuring good gas and liquid

distribution in the larger demonstration size reactors.

It is puzzling why Genoil did not market their proprietary mixing technology to

the established fixed-bed and possibly ebullated-bed process licensors rather than

developing their own fixed-bed process. If Genoil continues on the path they are

on, it will be a long road since they do not have significant expertise in heavy oil

hydrogenation, catalysts, flowsheet development, scale-up and reactor design.

The scale-up of the proprietary oil/hydrogen mixing device and ensuring that the

high level of hydrogen dispersion is achieved at higher capacities should not

present any significant issues.

Patents: Two Canadian / U.S. patents have been granted to Genoil. The most

important patent was filed in 1999 and granted in 2006. The patent does not

contain any supporting data for the advantage of the premixing of the hydrogen

with the feed oil. The application is not well written and does not substantiate the

claims for enhancements due to the hydrogen premixing. Another similar

Canadian patent application by a subset of the inventors in the Genoil patent

application is assigned to Canadian Environmental Equipment & Engineering (CE3) and was originally issued in 1998. CE3 was the original developer/owner of the forerunner of the Genoil Process. There is a recently granted patent (2009) assigned to one of the Genoil inventors, which concerns the proprietary mixing device.

R&D Facilities: Genoil operates a fairly large 10 BPD pilot unit located near Edmonton. Although this capacity appears high, many licensors rate their unit at the highest feasible throughput (i.e., low residence time). For heavy crude or bitumen, the pilot unit will process only 2 BPD or less. The unit designed for the Silver Eagle Woods Cross refinery in Utah was designed to process 1,200 BPSD of VGO and/or atmospheric bottoms. Although called a commercial facility by Genoil, it is best viewed as a demonstration plant. Genoil had an equity position and would have shared in the incremental revenues from the Utah plant.

Current Status: The management at Genoil is not technically oriented but instead is very aggressive marketing/PR oriented (e.g. "the next Microsoft"). Genoil is not interested in licensing their technology but in participating in commercial projects. As shown in *Attachment 1*, there are numerous press releases, announcements and marketing oriented papers released by Genoil. Some of the most important items involving the Genoil Technology are:

1. Project with Haiyitong Inc. (China) – An agreement with PetroChina was executed in mid-2003 for Genoil to test their Chinese crude. This work was not completed until late 2007. A MOU was signed in February 2006 to construct a 30,000 BPSD GHU Unit at the Hebei Zhongie Petrochemical Group (now Haiyitong Inc.) refinery in China. The GHU will desulfurize and hydrogenate the heavy Chinese crude and send the unconverted residue to gasification. In October 2006, an

LOI was executed for a 20,000 BPSD plant. The LOI called for Genoil to finance approximately 80% of the GHU capital cost (total = \$170 MM) and to share in the incremental revenues at a high rate (60%) until twice their costs are paid out. After that, Genoil will receive 10% of the GHU incremental revenues. Initial front end engineering was conducted in 2008 and the LOI was revised reducing Genoil's capital requirement to \$65 MM and also reduced their revenue sharing. To date (May 2010) Genoil has been unable to raise the funds to cover their current \$65 MM share of the project financing. The project is not mentioned in Genoil's 2009 year-end update. (see *Attachment 1*)

- 2. <u>Demo Plant</u> The 1,200 demo plant at the Silver Eagle refinery in Utah was announced in June 2004 and completion was slated for 2006. The plant feedstocks are sometimes reported as a VGO and other times as an atmospheric or even a vacuum bottoms. Genoil planned to participate in the incremental revenues generated by the project and has an equity position in the refinery modernization. The refinery was sold (GHU installation incomplete) and the new owners have requested to opt out of the agreement with Genoil.
- 3. <u>Steaua Romana</u> In August, 2006 Genoil and this Romanian refiner signed a MOU for use of the GHU Process (20,000 BPSD).
- 4. <u>LukOil</u> This major Russian refiner signed an agreement with Genoil in November 2004 to evaluate the upgrading of Komi crude. A pilot plant test was completed in 2005 and deemed successful by Genoil. A "commercial proposal" was provided to LukOil in October 2006 and Genoil is still awaiting their response.
- 5. <u>Surge Global Energy</u> A June 2005 press release announced a LOI between Genoil and Surge Global Energy to jointly build a 10,000 BPSD Upgrader. The feedstock is from the Sawn Lake field (near Peace River) in Alberta. Genoil will receive 30% of the net revenue stream of the proposed unit. The optimal level of upgrading, as indicated by the API gravity improvement, will be studied in the Genoil

pilot plant. A GHU product API as high as 34° is mentioned in the press release. The LOI indicated that the current agreement involved initiation of pilot and optimization studies and was not a commitment to construct a commercial facility. The upgrading project is completely stalled, opposed by the local Lubicon Nation, and only three wells have been drilled to date. Surge Global Energy does not mention Genoil on their website.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the Genoil Process is shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Aggressive Promotion	Newcomer to Upgrading	Data on Ural & Chinese
		Crudes
Patents Granted	Poor Patent Write-up	Effectiveness of Initial Mixing
		&Reduced Reactor Severity
Relatively Large Scale Pilot	Fixed-Bed Reactor Approach	Catalyst Requirements for
Plant	for Bitumen	High Metals Feedstock
Canadian Technology	Knowledge of Reactor Design	Ability to Raise Funds for
Company	and Scale-up	Chinese Project
Chinese Project	Knowledge of Product	
	Stability / Compatibility	
Level of Press Coverage	Loss of Silver Eagle Project	
	No Supporting Data for	
	Effectiveness of H ₂ Premixing	
	Requires External Hydrogen	
	Source	

The greatest strengths are the aggressive Genoil promotional tactics and the large-scale pilot plant. The project with the Chinese is important but will require extensive investment and development from Genoil. The greatest weaknesses are lack of critical data supporting their main feature (hydrogen premixing and enhanced kinetics) and the lack of experience with commercial development, scale-up and reactor design.

Best Applications: Although the first commercial installation (Utah–now cancelled) of the GHU Process was for the hydrotreatment of a heavy VGO, Genoil's target market is for heavy crude and bitumen upgrading. Genoil is targeting full upgrading (28–34° API SCO). In the last few years, Genoil has concentrated on applications and projects outside of Canada. This may speak to the inability to adequately process Canadian heavy oils and also to their lack of success in selling their technology and project financing arrangements to more technically astute Canadian and U.S. firms.

Summary: The GHU Technology could have some economic advantages over current fixed-bed and ebullated-bed technologies if the premixing of hydrogen is an effective phenomenon. No supporting data is available and the large majority of published information is PR. Genoil is "reinventing" the fixed-bed hydrocracking technology around their mixing invention. Using a fixed-bed reactor approach for moderate to high conversion is not applicable to most heavy oils, particularly Athabasca bitumen. If a GHU was ever to be constructed on heavy feedstock, an extended period of time and additional money would be required to start-up and to implement modifications to meet process performance expectations. There is a chance that the project in China project may go ahead if Genoil is able to raise the required investment, however it is believed that the Genoil commercialization effort will not be successful.

Eni Slurry Technology (EST)

By Eni S.p.A.

Go To: Publications Patents

Process Name: Eni Slurry Technology (EST)
Process Type: Slurry-Bed Hydrogen Addition

Company: Eni S.p.A, Italy

Public Italian Company

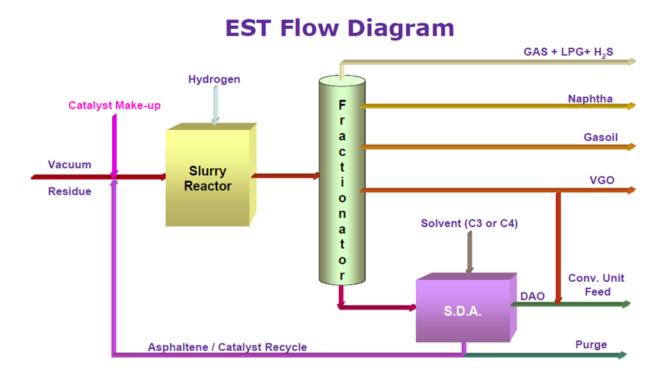
Website: http://www.eni.it/en_IT/home.html

Process Overview & Objective: The Eni Slurry Technology (EST) is a slurrybed catalytic hydrocracking technology similar to that licensed by Headwaters Heavy Oil (HCAT), Mobis Energy (HRH), UOP (Uniflex) and Chevron (VRSH). The process is classified as a full conversion process since it operates at high residue conversion, requires hydrogen and catalyst, and the product SCO will contain minimal asphaltenes. The key features of the EST Process are: 1) hydrocracking of the feedstock residue at high temperature and pressure using a non-supported, micro-sized catalyst, 2) atmospheric and vacuum distillation of the conversion products, 3) routing of the unconverted vacuum residue to a propane/butane solvent deasphalting unit (SDA), and 4) recycle of a large portion of the catalyst-containing asphaltenes back to the EST Reactor. For a Western Canadian feedstock application, the SCO product is comprised of the straight-run and conversion distillates and the DAO from the SDA Unit. There appears to be various versions of the process including omission of the SDA and recycle step and a configuration with an upstream SDA unit with separate hydrocracking of the DAO and asphaltenes.

The EST concept originated in the late 1980's with the primary process development occurring in the last 10 years. The development path has included initial catalyst screening, micro reactor and bench scale tests, pilot plant construction and testing, and the operation of a large 1,200 BPD demonstration unit. A 23,000 BPSD commercial EST facility is currently under construction at an Eni affiliate refinery with start-up scheduled in 2012.

The slurry catalyst is generated in situ and is recyclable, resulting in only a small net catalyst make-up. The active metal utilized in the process is molybdenum although some of the nickel/vanadium from the heavy oil feedstock is included with the recycled active catalyst metal and may provide additional catalytic activity.

A simplistic flow diagram for the EST Process is shown below. The vacuum residue from the heavy oil or bitumen is the feed to the process. The residue plus hydrogen and make-up catalyst are fed to the slurry reactor. According to Eni, the reactor has a high degree of backmixing and operates at approximately 770°F and



2,350 psia. This temperature is fairly low considering the overall claimed conversion. To attain high residue conversion at the low reactor temperature, significant residue recycle and a long reactor residence time is required. This

recycle will result in a high product separation and distillation design capacity and large EST Reactors for a given feedstock throughput. The EST Reactor effluent is sent to product separation and fractionation including both atmospheric and vacuum stills. The vacuum residue is routed to a propane or butane deasphalter (SDA Unit) to remove the unconverted asphaltenes and the slurry catalyst from the EST heavy product. The larger portion of the SDA asphaltene product is recycled to the EST Reactors. This will aid in increasing both the vacuum residue/asphaltene and catalyst concentrations in the reactor. A relatively small purge of asphaltenes is claimed. The purge rate is set to eliminate the metals removed from the feedstock and to attain the overall vacuum residue conversion level. It is unknown if the asphaltene/catalyst recycle undergoes any processing before recycling to the EST Reactors.

For a Western Canada application of the EST Process, the SCO is comprised of the straight-run and conversion distillates and the DAO from the SDA Unit. The overall conversion level reported by Eni (+95%) assumes that the DAO is converted material. Since the SDA Unit is fed by primarily vacuum residue boiling range material, the DAO will be 100% vacuum residue and will end-up in the SCO product. With DAO accounted for as vacuum residue, the actual residue conversion level is in the range of 80-85%.

Claims: The important Eni claims for the EST Process center on the activity of the micro-sized catalyst, the ability to be recycled, and the high conversion levels which can be achieved. High levels of HDS, HDN, and CCR and metals removal are also claimed. The EST Reactor is claimed to have a high degree of backmixing as evidenced by a 6°F axial temperature gradient in the demonstration plant reactor.

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For an Athabasca bitumen feedstock, Eni has indicated an SCO yield of approximately 113 V% on feed with the following inspections API gravity: 27°, sulfur: 0.94 W%, nitrogen: 0.24 W%, CCR: 0.5 W% and nickel plus vanadium: < 1 Wppm. This SCO will meet Canadian pipeline specifications and should obtain just a small price discount relative to WTI. This level of SCO volumetric yield on vacuum residue feed is typical of a catalytic hydrocracking process operating at high conversion. Early EST publications indicated a chemical hydrogen consumption of 800 SCF/Bbl; this is judged to low and a value of at least 1,500 SCF/Bbl is expected.

The reported EST conversion levels of 95-98% consider that SDA DAO is converted product and are consistent with the small (2-5%) asphaltene/residue purge rate. Since the DAO is vacuum residue, the actual vacuum residue conversion level is approximately 80-85%. This reported high conversion but inclusion of residue (i.e., DAO) in the SCO is large advantage for the EST Process compared to other slurry catalyst processes and is a result of the novel processing scheme. Additionally, the temperature in the EST Reactors is relatively low and will therefore aid in the production of a stable product even at 80-85% conversion. This low reactor temperature operation however, requires a long residence time and significant catalyst concentration. The long residence time is obtained by a low reactor space velocity. This is evident by the 20,000 BPSD EST commercial plant requiring two maximum-size high pressure reactors.

To obtain the required reactor catalyst concentration of 1,500 to 5,000 Wppm (from Eni patent application), a recycle of asphaltenes containing the catalyst from the SDA Unit is required. The recycle rate is not reported by Eni but is estimated at approximately 0.3 to 0.5 of the fresh feedrate. This asphaltene recycle stream (same composition as process purge) will be difficult to process and pressurize and

may require fluxing with a lighter material in order to be pumpable. Because of the recycle, the downstream vessels in an EST Unit will therefore be designed for approximately 50% higher flowrate than the fresh feedrate. For example, a 20,000 BPSD EST Unit will require a 30,000⁺ BPSD atmospheric still.

Even with the reduced EST Reactor severity, the stability of the unconverted

vacuum residue is in question at these high conversion levels. In a commercial

EST Plant, the asphaltenes are nearly extincted; however the material fed to the

atmospheric and vacuum stills will contain asphaltenes and may possibly be an

unstable mixture. This may result in fouling in the various vessels and significant

unit downtime. This will be particularly evident in the vacuum still and the SDA

Unit.

In addition to the process configuration discussed above, the Eni patent and patent

applications also reveal other configurations which utilize the EST Reactor and

catalyst. These include the omission of the downstream SDA Unit, resulting in a

process similar to HRH, VRSH and HCAT, and a scheme where the SDA Unit (C₄

or C₅ solvent) is upstream of the EST Reactors. In the latter case, there are

separate EST Reactors (and operating conditions) for the DAO and asphaltene

streams and a common product distillation area.

Product & Waste Issues: There are no data to evaluate the stability and

compatibility of the EST SCO. However, since the final SCO product does not

contain any feedstock or conversion plant asphaltenes, it should be stable. The

non-residue liquids from the EST Process should be similar in quality to those

from an ebullated-bed unit such as the Husky Lloydminster Upgrader or Syncrude

Canada Plant.

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For higher conversion operation, there are concerns with the stability of the EST unconverted vacuum residue. The EST unconverted residue is not included in the SCO product; however vacuum residue instability may result in fouling issues in the commercial vacuum tower and in the SDA Unit. This issue should have been addressed in the EST demonstration plant.

The EST Process asphaltene/catalyst purge presents a unique disposal issue. This stream is reported to be approximately 2 W% of the heavy oil feedstock rate and for an Athabasca bitumen application will contain approximately 1.2 W% catalyst and 2.5 W% contaminant metals (primarily nickel, vanadium and molybdenum). In an Eni publication, the purge is routed to a "Purge Treatment Plant" which produces an intermediate sulfur fuel oil and a solids stream. The solids would be a valuable stream for a metals reclaimer. Although the rate of this purge stream is small and has a negative value, it may require significant investment to properly be disposed of.

Scale-up: The EST Process has been scaled-up from the micro reactor, bench-scale, pilot and demonstration plants. The 1,200 BPD demonstration plant should have addressed and solved all scale-up issues. Details for the demonstration plant history have not been made public. There was a lack of published progress reports and press releases which typically tout significant successes.

Important scale-up issues would include gas hold-up (much higher in commercial reactor) which decreases the liquid phase reaction rates, fouling in downstream vessels, particularly the vacuum still, and achieving an equilibrium asphaltene recycle rate resulting in a steady state level of catalyst activity. If an initial scale-up to the demonstration scale is successful and critical items are properly addressed, then the additional scale-up from the demonstration facility to a

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commercial size should not be difficult.

Patents: Two U.S. patents relative to the EST Process were granted, one in 1999

and the second in April 2010. The 1999 patent describes the EST Process as

discussed above. The latest patent describes the EST Process version where the

SDA is located upstream and the DAO and asphaltenes are hydrocracked in

separate EST Reactors. Nine patent applications related to EST were found with

some dating back to 2003. The applications cover general process configurations

which includes slurry catalyst hydrocracking, distillation and solvent deasphalting

steps. For example, several of the applications indicate that the fresh vacuum

residue can be split between the EST Reactors and the SDA Unit. This is not the

case for the process as described in the Eni publications and is assumed to be used

in the commercial plant currently under construction. The patent applications

describe the catalyst type, usage rate and operating conditions in the EST

Reactors.

If the above intellectual property search is accurate, it is surprising that Eni has not

obtained patent coverage and has not issued patent applications covering finding

from the demonstration plant operation. Typically this would include

equipment/device related patent applications.

R&D Facilities: ENI has developed the process based on the operation of micro

reactor, bench, pilot, and demonstration plants. The scale (feed throughput) of the

pilot unit operated in the 2000-2003 timeframe was 0.3 BPD. It is assumed that

the pilot is still available for feedstock and optimization studies. It is not known if

catalyst regeneration and recycle are included in the pilot unit.

The EST demonstration plant is located at Eni's Taranto refinery in Italy. The unit

is termed the CDP (Commercial Demonstration Plant) and was constructed by

Snamprogetti. The CDP includes all of the features utilized in a commercial EST facility. The plant can process 1,200 BPD of feedstock; it is unknown if this capacity is on a crude or atmospheric/vacuum residue basis. The first test was performed in late 2006. Feedstocks evaluated include Athabasca, Ural and visbreaker residue. Over 230,000 Bbl of residue have been processed in the CDP.

Current Status: Some of the most important items involving the EST Process are discussed below:

1. Commercial Plant – A 23,000 BPSD commercial EST Unit is currently under construction at Eni's Sannazzaro refinery in the Po valley (Italy). Details as to the feedstock and conversion level are not available. The EST Reactors will be 2,000 MT and are reported to be of maximum size. The reactors will be shipped as rings as field welded prior to erection. A September 2012 start-up is planned. The installation of the EST Unit is part of a planned refinery expansion. The feed to the unit may be Ural residue, visbreaker residue or a combination thereof. This is evidenced by these feedstocks being processed in the demonstration unit. The refinery also includes a new gasifier (2006) to which the visbreaker residue is current fed. It is unknown if and how the EST is integrated with the existing visbreaker and gasifier.

Flow diagrams for the Sannazzaro unit have not explicitly shown the SDA Unit which would be fed the unconverted residue nor and recycle to the EST Reactors. Instead a PTU (Purge Treatment Unit) is indicated. There is a possibility that the SDA unit and the recycle of catalyst and asphaltenes is not included with this initial EST commercial plant.

2. <u>Republic of Congo Project</u> – In May 2008, Eni executed an agreement with the Republic of Congo to evaluate the newly discovered heavy tar sands in that country. After an initial exploration phase, the 2nd phase of the project will evaluate a 3-4 month operation with the extracted oil in

- the CDP. The last phase includes a commercial EST Plant at the Point Noire refinery.
- 3. <u>Demo Plant</u> The 1,200 BPD demo plant was constructed in the Taranto refinery beginning in 2003. The unit started-up in November 2005 and has conducted several long-term tests on feedstocks such as Ural and Athabasca bitumen.
- 4. <u>Agreement with Venezuela</u> In March 2008, Eni and PDVSA signed an agreement to establish a joint venture to study and eventually process 300,000 BPD of Orinoco heavy oil with an initial 30,000 BPSD to be studied. The joint venture will be 60% PDVSA and 40% Eni. The agreement also allows Eni to make the EST Process available for upgrading the Venezuelan heavy vacuum residue.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the EST Process is shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Good Development History	Downstream Fouling Issues at High Conversion	Net Catalyst Cost
Moderate Reactor	High Hydrogen	Actual Catalyst Usage with
Temperature	Consumption	Bitumen Feedstock
Demonstration Plant	Low Feedstock for Given	Objective Economic Comparison
Operation	Max Reactor Size	with Ebullated-Bed and Coking
Commercial Plant (20,000	High Light Gas Yields	Steps for Catalyst Preparation and
BPD) under Construction		Recycle
High Conversion (inc.	Catalyst (Ma) Cast	Demo Plant Issues and Required
DAO) Capability	Catalyst (Mo) Cost	Modifications
Minimal Bottoms to	High Initial Investment	
Disposal of	Tilgii ilittai ilivestillelit	
High Diesel Yield		

The greatest strengths are excellent development path followed concluding in the current commercial plant under construction. Relative to other slurry catalyst processes, EST operates at lower severity (conversion) since the DAO product is

included with the SCO. Major weaknesses are the estimated high initial investment which is partially a result of a low feedstock throughput per reactor train, the relatively high light gas yields and related hydrogen consumption, and the possible high cost of the molybdenum catalyst make-up.

Best Applications: With the capability of attaining high conversion of vacuum residues, the preferred application of the EST Process would be for producing a bottomless SCO. This high conversion will require high initial investment and operating costs and would be preferred when there no disposition for the unconverted residue or if the residue or purge carries a large negative value. Additionally, operation without the asphaltene/recycle may be consistent for lower conversion operations where the unconverted material is sent to a gasifier for hydrogen production. With the EST Process, a high yield of sour SCO with an API gravity of approximately 27° could be produced without any secondary hydrotreating. This would provide a large revenue stream for an upgrader but would require a high light to heavy oil margin to return a reasonable profit.

Summary: The EST Process is one of the many high conversion slurry catalyst processes and will the first to be commercialized. Its success is a result of the process concept and the excellent process development strategy. The application of slurry catalyst technology at very high conversion (>90%) is not technically or economically attractive as a result of high hydrogen consumption, high investment cost and disposal issues relating to the poor quality purge stream. The EST Process actually operates at milder vacuum residue conversion (80–85%) but includes the SDA DAO in the SCO product. This results in a net purge stream rate of 2-5 % of the heavy oil feedrate, indicative of a 95-98 % conversion process.

The profitability of the process, given the estimated high investment and operating costs, will be highly dependent on the market value of the EST SCO. Application of the EST Process in Western Canada is possible, although the high required investment and operating costs are large barriers, particularly since late 2008.

HCAT Technology

by Headwaters Heavy Oil, LLC

Go To: Publications Patents

Process Name: HCAT Heavy Oil Hydrocracking Technology

Process Type: Slurry-Bed Hydrogen Addition

Company: Headwaters Heavy Oil, LLC, Lawrenceville, NJ

U.S. Public Company

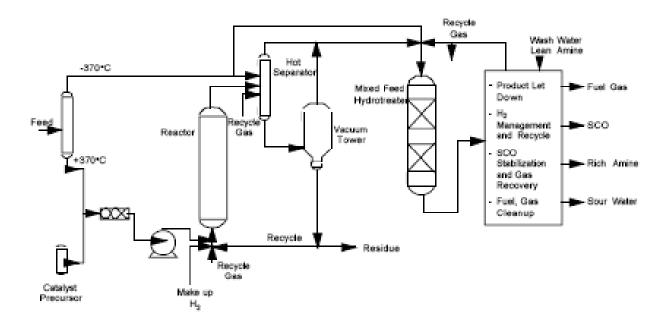
Website: http://www.htigrp.com/

Process Overview & Objective: The HCAT Process (formerly the (HC)₃ Process) is a full upgrading residue catalytic hydrocracking technology. The key element of the process is a unique molecular-sized proprietary catalyst which is claimed to provide enhanced catalytic performance and reduced investment and operating costs. The process was originally developed by the Alberta Research Council / AOSTRA in the late 1980's. Process licensing rights were sold to Headwaters in 2002. Headwaters Heavy Oil owns and operates the former HRI (now Axens North America) R&D Center in Lawrenceville, NJ.

Headwaters Heavy Oil significantly improved the original ARC/AOSTRA Process through extensive pilot plant studies including the evaluation of several commercially viable feedstocks. This has resulted in advances in the catalyst preparation step and improvements in the process performance. Headwaters also studied the addition of the HCAT catalyst to an ebullated-bed reactor and determined that it improved process performance (HDS, etc.) and increased the maximum residue conversion in the ebullated-bed units. The latter item can allow an ebullated-bed plant to operate at higher residue conversion (more profitable operation due to higher distillate yields) with minimal or acceptable levels of fouling resulting in long unit run lengths. In 2009, Headwaters and Criterion Catalysts formed a technical alliance to offer the HCAT Technology in conjunction with Criterion's ebullated-bed catalysts.

The HCAT Process utilizes an entrained or well-mixed type reactor and operates at high pressure and temperature. The process operates at high levels of residue conversion, typically greater than 80%. It is a full upgrading process with the small quantity of unconverted vacuum residue containing the metals in the catalyst precursor. This unconverted residue has low utility and must be combusted or routed to a gasifier.

A process flow diagram, taken from in the Headwaters website, is shown in the figure below.



The process configuration shown above includes optional integrated secondary hydrotreating of the HCAT liquids in order to further reduce the sulfur and other contaminants levels in these products. The HCAT catalyst precursor (molybdenum-based) is added to the heavy feed, sent to a mixer and then pumped into the HCAT Reactor. The mixed-phase hydrotreater further upgrades the HCAT liquids, plus the feed materials which boil below approximately 700°F. The hydrotreater operates at approximately the same pressure as the HCAT

Reactor but at reduced temperature.

Claims: The major claim is that the high activity of the catalyst results in

improved hydrogenation and cracking reactions in the HCAT Reactors such that

the reactor operating conditions (primarily hydrogen partial pressure) can be

reduced relative to existing commercial processes. The high catalyst activity is a

result of the intimate dispersion of the molybdenum sulfide in the residue

feedstock. Headwaters claim that the catalyst is mixed at the "nano" level.

Relative to the ebullated-bed processes, the HCAT Process can more easily attain

higher levels of residue conversion, with higher liquid yields (i.e., more SCO).

Relative to other slurry catalyst processes (EST, HDH Plus, HRH, and VRSH), the

HCAT Process claims intimate dispersion of the molybdenum catalyst in the

heavy oil feedstock and can therefore operation with a lower rate of catalyst usage.

This will result in lower operating costs and alleviate the need for expensive and

complex catalyst recovery, regeneration and recycle.

Product & Waste Issues: The spent HCAT catalyst is removed with the heavy

liquid product and will have high concentrations of spent catalyst and metals at

high conversion levels. For example, at 90% conversion, the heavy HCAT liquid

will contain 9 times the concentration of catalyst that was added in the feed.

Gasification of the bottoms, as was planned for the North West Upgrader, will

help to alleviate this issue since the catalyst metals are removed in the gasifier.

The quality of the HCAT liquid products are inferior to that from an ebullated-bed

or fixed-bed process and will require more downstream hydrotreating.

Scale-up: The scale-up from the HCAT Process pilot unit (10-15 gal/Day) to a

commercial facility was partially completed in late 2005 when the HCAT catalyst

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was utilized in a commercial ebullated-bed reactor system. The complete HCAT Process has not been commercialized. An intermediate-scale demonstration plant is not planned.

Patents: – There are four patents granted for the HCAT Technology. The original (HC)₃ patent was issued in 1996 and was assigned to AOSTRA. The patent contains significant background on asphaltene chemistry and the formation of coke and precipitated asphaltenes. Other granted patents cover application of the HCAT additive to fixed and ebullated-bed reactor systems. HCAT patent discussions directly illustrate the effect of the HCAT additive since data are shown with and without the HCAT catalyst. Other current patent applications (3 filed in 2009) are specific to the system and procedures for preparation of the HCAT catalyst and also cover catalyst precursor manufacture.

R&D Facilities: Headwaters operates a 10-15 gal/day pilot unit located in Lawrenceville, NJ. This is the same pilot unit which has been successfully used to establish commercial design bases for ebullated-bed reactor plants.

Current Status: Headwaters is active in commercializing both the HCAT Process and the HCAT catalyst. The current emphasis is on selling the HCAT catalyst as a supplement for ebullated-bed commercial plants. The HCAT Process is available for license by the refining industry. Some of the most important items involving the technology are:

 Alliance with Criterion – In April 2009, Headwaters and Criterion Catalysts & Technologies formed a technical alliance which allows Criterion to offer the HCAT catalyst additive in conjunction with Criterion's ebullated-bed catalysts. The press release claims increased

- conversion, less fouling and improved product quality with the use of the HCAT additive.
- 2. Catalyst Commercial Tests The HCAT catalyst was added to a commercial ebullated-bed reactor in late 2005 to assess its effect on process performance (conversion, sulfur removal, product stability, etc.) The test was deemed a success in a January 2006 Headwaters news release although detailed comparative and required actual results were not published. Further tests were conducted at a second U.S. refinery (2 trials) in 2006. A fourth trial was scheduled for December 2007 at the new Neste LC-Fining Unit in Finland but no announcement was published. The results of the HCAT ebullated-bed trials are highly touted by Headwaters but the industry response has not been very positive.
- 3. Northwest Upgrader The HCAT Process was selected by North West Upgrading for use at the planned North West Upgrader in Alberta. The upgrader will purchase various heavy oil feedstocks and was to be the first independent refinery to process bitumen and heavy oil in Alberta. The unconverted HCAT Process vacuum residue was to be sent to a gasifier. Based on the ability to raise capital, North West Upgrading eventually selected a commercial ebullated-bed process (LC-Fining) instead and cancelled the HCAT Process license. North West Upgrading may eventually utilize the HCAT catalyst in the ebullated-bed reactors once the plant is started-up and operated.
- 4. <u>Pilot Plant</u> In recent years, the HCAT pilot plant has operated nearly continuously evaluating candidate feedstocks. This is a good signal of company commitment and industry interest.

Strengths / **Weaknesses** / **Unknowns:** A table summarizing the strengths, weaknesses and unknown factors of the HCAT Process and the HCAT additive (catalyst) are shown on the following page.

Strengths	Weaknesses	<u>Unknowns</u>
Good Patents and	Newcomer to Upgrading	Real Reductions in Reactor
Applications	10 0	Severity
Low Catalyst Usage Rate	No Demonstration Scale Unit	Economics Relative to
and Operating Cost		Ebullated-Bed
Operating Pilot Plant	Loss of North West Upgrading	Actual Results of Commercial
	License	Test at Ebullated-Bed Plant
Commercial Catalyst Tests	High Pressure, High H ₂ Usage	
in Ebullated-bed System	Tingii Tiessure, Tingii Ti ₂ Osage	
Alliance with Criterion	Reduced Value of Product	
	Containing Spent Catalyst	

The strongest strengths are the claimed low catalyst usage rate and resulting operating cost, and the trials in commercial ebullated-bed systems. The strongest weaknesses are lack of a demonstration plant, the high pressure/temperature operation, and the low utility of the unconverted vacuum residue product.

Best Applications: The best application of the HCAT Technology is for heavy oil upgrading (full upgrading) with the unconverted material sent to a gasifier for hydrogen and/or power production. This was the configuration for the planned North West Upgrader. With full upgrading using the HCAT Process, a SCO with an API gravity of $32 - 38^{\circ}$, would be produced.

The addition of HCAT catalyst to an existing ebullated or fixed bed reactor systems may become an important application and help to market the HCAT Process. A highly successful trial, resulting in continuous use of the additive, is required to significantly advance the HCAT Technology.

Summary: The HCAT Process is one of the many high conversion slurry catalyst processes, none of which have been commercialized, although a commercial EST Plant is currently under construction. Its largest advantage is the low catalyst

injection rate due to intimate mixing of the feedstock and additive. I general, the application of slurry catalyst technology at very high conversion (>90%) is not technical or economically attractive as a result of high hydrogen consumption, high investment cost and the extremely poor quality of the unconverted residue. Application at milder conditions (75-80% conversion) with the unconverted residue routed to a gasifier may be the preferred configuration and would have a greater potential for eventual commercialization.

Heavy Residue Hydroconversion (HRH)

Technology

by Mobis Energy

Process Name: Heavy Residue Hydroconversion (HRH) Go To: Publications Patents

Process Type: Slurry-Bed Hydrogen Addition

Company: Mobis Energy, Inc., Calgary, Alberta (N.A. Licensor)

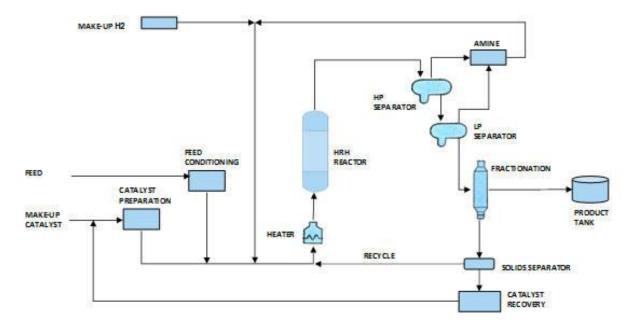
Canadian Private Company

Website: http://mobisenergy.com

Process Overview & Objective: The HRH Process is a slurry-bed catalytic hydrocracking technology not significantly different from that licensed by Headwaters Heavy Oil (HCAT). The process is licensed in North America by Mobis Energy whom is collaborating with the Research Institute of Petroleum Industry (Iran) and a Russian firm, NTI Company. The HRH Process was originally developed in Russia. The key element of the process is the effective use of a unique molecular-sized (nano) catalyst which is claimed to provide enhanced catalytic performance and reduced investment and operating costs. The catalyst active metal is also recyclable, resulting in only a small net make-up. The active metal utilized in the process is molybdenum although some of the nickel from the heavy oil feedstock is included with the recycled active catalyst metal.

The vacuum residue from the heavy oil is the feed to the process. The major HRH Process claims are the capability to attain deep vacuum residue conversion (90-95%) with moderate/high HDS and HDN. This claim is for the processing of heavy crudes including Athabasca bitumen at pressure levels 70% of those used conventionally. This would indicate operation at approximately 1,900 psi and a hydrogen partial pressure of 1,400 psi, although 1,000–1,450 psi total pressure is claimed by Mobis Energy.

According to Mobis Energy, Russia has been utilizing the HRH Process since 1991 (200 BPD demonstration unit) although with a larger-sized and a less active catalyst. A typical process flow diagram for a refinery utilizing the HRH Process is shown on the following page. Key features are: 1) the recycle of heavy liquid to the HRH Reactor, 2) the catalyst recovery system which produces recycle catalyst active metal, ammonium sulfate and metal oxides. Not shown on the block flow diagram is a block where "chemicals" are used with the recycled active metals before recycling to the HRH Reactor.



The specific steps for the process with an emphasis on catalyst preparation and recycle, taken from the HRH Process patent are:

- 1. Addition of an aromatic oil, such as a FCC cycle oil, to the heavy oil feedstock at a rate of 0.5 to 3.5 W% of the feed.
- 2. Stabilizing the mixture in Step 1 with a polar compound such as acetone or diethyl keton at a rate of 0.001 to 0.01 W% of the feed.

- 3. To 5–10% of the product from Step 2 add aqueous ammonium paramolybate (APM) to attain a required ratio of feed/water/APM
- 4. Mixture from Step 3 is homogenized via mixing and heating.
- 5. Entire heavy oil feed plus liquid from Step 4 is sent to the HRH Reactor which operates at 400-500°C and 1-15 MPa pressure with hydrogen addition. Molybdenum concentration is the reactor is 50-500 Wppm.
- 6. Products are distilled in atmospheric and vacuum stills; the heavy vacuum residue product (520°C⁺) is combined with 3–10% of the total gas oil and is filtered.
- 7. The low solids containing filtrate from Step 7 is recombined with the feedstock. The solids are combusted with air.
- 8. The ash from Step 7 is extracted with ammonium carbonate to recover the molybdenum and a portion of the nickel from the feedstock. The recovered material is recycled to the catalyst preparation step.
- 9. The flue gas from Step 7 is treated with ozone (reduce NO_x) and ammonia with the SO_x converted to ammonium sulfate.

Claims: The important claims for the HRH Process center on the nano-size catalyst and the technology to burn the unconverted vacuum bottoms and recover and recycle the catalyst active metals. In the catalyst recovery block, the filtered solids from the unconverted vacuum residue are burned to produce steam. The ash product is then processed, via leaching, to recover the catalyst active metal. Mobis Energy claims that the combustion/recovery block is completely designed (by a Lurgi affiliate) and will perform as estimated. In a commercial plant, filtration is generally not feasible; it is not known how this separation will be accomplished in a commercial HRH Process facility. It is unknown if the catalyst recovery unit has been demonstrated in the HRH pilot plant, however it is included in the 200 BPD demonstration plant which has been reported to be constructed and operated.

Other slurry catalyst processes have reported similar level of process performance (residue and asphaltene conversion, HDS) but not at the reduced pressure levels and small net catalyst make-up rate (0.01 Kg/Bbl) claimed by Mobis Energy. A portion of the heavy vacuum gas oil from the process is recycled back to the HRH Reactor and results in lighter yield selectivity. This will also help to completely remove any asphaltenes which are present in the heavy ends of the VGO product.

The major claim is that the HRH catalyst diffuses onto the surfaces of the asphaltene molecules where efficient hydrocracking can occur. According to the HRH Process patent, the additive is ammonium paramolybate which is water soluble. The process operates at fairly high temperature (430–490°C) which is required to obtain the high levels of residue conversion. The stability of the unconverted vacuum residue may be in question at these high conversion levels, particularly with the low hydrogen pressure operation. In a commercial HRH Plant, the vacuum residue is extincted; however an unstable mixture containing the unconverted residue may cause affect fouling in the various downstream vessels such as the atmospheric and vacuum stills and the catalyst recovery plant.

In a specific commercial estimate which upgrades 10,000 BPSD (a low feedrate) of a 4 W% sulfur vacuum residue, Mobis Energy reports a 104 V% yield, excluding the yield of unconverted bottoms. This level of SCO volumetric yield on vacuum residue feed is typical of a catalytic hydrocracking process operating at 95% conversion. Hydrogen consumption (chemical plus solution) of 1,830 SCF/Bbl and just 0.02 Lb/Bbl catalyst make-up is estimated. A large range of light gas yields (5-10 W%) is provided indicating that the gas yields may be high. The HRH SCO product is reported net of the vacuum bottoms (520°C+) which are consumed in the catalyst regeneration step. Only 60-80% HDS is reported indicating the relatively thermal nature of the process.

Product & Waste Issues: There are no data to evaluate the stability and

compatibility of the HRH SCO. However, since the SCO does not include the

520°C⁺ unconverted vacuum residue, it should be stable. The non-residue liquids

from the HRH Process should be similar in quality to those from a single-stage

ebullated-bed unit such as the Husky Lloydminster Upgrader or Syncrude Canada

Plant.

For higher conversion operation, particularly with the relatively low hydrogen

partial pressure claimed, there are concerns with the stability of the HRH

unconverted vacuum residue. The unconverted residue is not included in the SCO

product; however vacuum residue instability may result in fouling issues in the

commercial atmospheric and vacuum towers and in the catalyst regeneration plant.

This issue may be alleviated as a result of the very high claimed HRH asphaltene

conversion and if the HRH catalyst is as active as claimed.

The HRH Process catalyst regeneration plant combusts the filtered solids from the

unconverted residue to provide heat (steam product) and a waste metal-oxide (ash)

product. The metal oxides contain the nickel and vanadium in the heavy oil

feedstock and would valuable to a metals reclaimer. The flue gas from this

combustion would require scrubbing or the combustion performed in a fluidized-

bed combustor.

Scale-up: The HRH Process has been scaled-up in the laboratory to a 2 BPD pilot

unit. The 200 BPD demonstration plant (reported to be operating in Iran) should

be able to address and solve the large scale-up issues. The issue of gas hold-up

may be a problem in the demonstration plant and will result in higher reactor

temperature or less feedstock capacity per HRH Reactor. If an initial scale-up to

the demonstration scale is successful, then the additional scale-up from the

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demonstration facility to a commercial size should not be difficult.

Patents: A U.S. patent was granted to the Research Institute of Petroleum Industry

(Iran) and a Russian firm, NTI Company in September 2009. The HRH patent is

fairly descriptive of the technology and the much of the discussion above was

based on the patent contents. Small scale 40 L/Day studies were the basis of the

patent claims.

R&D Facilities: HRH reports that 40 L/D (in Russia) and 2 BPD (in Iran) pilot

plants are available. It is not known if the catalyst regeneration and recycle steps

are included in the 2 BPD Unit. The 40 L/D Unit, located near Moscow, would be

available to prospective North American projects. A 200 BPD demonstration plant

was constructed at the Bandar Abbas refinery in Iran and according to the Mobis

Energy website, as been in operation. This unit includes the catalyst regeneration

step and should be capable of conducting relatively long-term tests to insure its

validity. There are no published data from the demonstration facility.

Current Status: Limited public information concerning the HRH Process is

available. The introduction of a North American licensing affiliate (Mobis

Energy) was announced in 2006. Since then, three similar Mobis

papers/presentations were published in Canada. Some of the most important items

involving the HRH technology are:

1. <u>Demo Plant</u> – The 200 BPD demo plant in Iran is presumably operating

although no data are available. This unit is a major investment and

should have all the features of a commercial unit. Its operation and

subsequent further development of the process will be critical to the

future of the HRH Process. The design feedstock for the demonstration

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- plant is presumably the Soroush heavy oil since it will be located at the Soroush area.
- 2. Soroush Refinery Plant A 10,000 BPSD commercial plant is reported to be licensed and in the design phase. Basic engineering has been completed. The location is given as in the Persian Gulf region. Soroush is a heavy Iranian crude oil (API gravity =18°, sulfur = 3.3 W%). No other details are available. The feedstock capacity of this first commercial installation is low and would not have favorable economic for a Western Canadian application

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the HRH Process is shown below.

<u>Strengths</u>	Weaknesses	<u>Unknowns</u>
Simple Reactor	Fouling Issues at High Conversion	Scale-Up Issues
Similar to Other Slurry	Combustion in Catalyst	Actual Catalyst Usage and
Catalyst Processes	Regeneration Step	Effectiveness of Recycle
Pilot Plant Availability	Demo Plant in Iran	Net Catalyst Cost
Commercial Plant (10,000	Knowledge of Product Stability /	Catalyst Requirements for
BPD) in Design	Compatibility	High Metals Feedstock
Demo Plant Operating in 2008	Not Commercialized 16 Yr after S/U of 200 BPD Russian Plant	Actual Pressure Reduction
Low Pressure and Low	Requires External Hydrogen	Maximum Single Train
Catalyst Usage Claims	Source	Capacity
	Commercial Filtration of	
	Unconverted Vacuum Residue	

The greatest strengths are the catalyst activity claimed leading to lower operating/design pressure design and the low catalyst usage rate. Additionally, the current pilot plants, operating demonstration plant, and commercial plant in design indicate aggressive commercialization. The greatest weaknesses are the Russian or Iranian ownership and initial installations, and the technical risks associated

with the catalyst regeneration step. Mobis Energy has not been aggressive in introducing and marketing the process in North America. The catalyst regeneration step, which includes complete elimination of the heavy unconverted vacuum residue, has the highest level of technical uncertainty.

Best Applications: The best application of the HRH Technology may be for heavy oil upgrading with the unconverted residue sent to a gasifier for hydrogen production. This would avoid some of the issues relative to the catalyst regeneration step (combustion of bottoms). With full upgrading using the HRH Process, a sour SCO with an API gravity of approximately 32° could be produced without any secondary hydrotreating. If based on Western Canadian feedstock, the SCO would contain approximately 2 W% sulfur, but would not contain any unconverted vacuum residue or asphaltenes. Assuming sufficient hydrogenation via the hydrogen partial pressure and catalyst activity, the HRH liquids (distillates plus VGO) which comprise the SCO, should be stable and compatible.

Summary: The HRH Process is one of the many high conversion slurry catalyst processes, none of which have been commercialized although the first EST plant is currently under construction. The application of slurry catalyst technology at very high conversion (>90%) is not technical or economically attractive as a result of high hydrogen consumption, high investment and operating costs and the extremely poor quality of the unconverted residue. Application at milder conditions (75-80% conversion) with the unconverted vacuum residue routed to a gasifier for hydrogen production may be the preferred configuration and would have a greater potential for eventual commercialization. The HRH Technology could have economic advantages over current fixed-bed and ebullated-bed technologies if the catalyst is highly active as touted and its cost is not prohibitive. The ownership of the HRH Process presents an issue for many possible clients.

When available, HRH Process yield and performance data from the demonstration plant should be analyzed to further investigate the merits of the technology.

OrCrude Process

By OPTI Canada

Process Name: OrCrude Process Go To: Publications Patents

Process Type: SDA + Thermal Cracking

Company: OPTI Canada, Calgary, Alberta, parent firm: Ormat Industries

Public Canadian Company

Website: http://www.opticanada.com/

Process Overview & Objective: Unlike many of the new upgrading processes investigated, the OrCrude Process is not a new unique reactor and/or catalyst technology developed for the heavy oil industry. It is a combination (integration) of three well-known process steps, atmospheric/vacuum distillation, solvent deasphalting and thermal cracking. The products from the OrCrude Process are:

1) a very heavy asphaltene stream which is sent to a gasifier to produce hydrogen, steam, syngas and power and 2) a low API gravity raw SCO which is sent to a high-pressure hydrocracker to produce the final SCO. The SCO does not contain any vacuum residue and the process is thus considered full upgrading. The gasifier and hydrocracker are not part of the OrCrude Process but would be included in a typical Upgrader. An OrCrude based heavy oil Upgrader will not require any natural gas. The Upgrader hydrocracker is a licensed technology and produces 34-40 ° API gravity SCO with high associated hydrogen consumption. The process produces a relatively low SCO yield and a high quantity of excess energy (steam, power, and raw syngas) and fits well with a SAGD project.

Claims: The major claim is that the integration of the three process steps (distillation, solvent deasphalting and thermal cracking) and the selection of optimal operating conditions results in an economic configuration for processing heavy crudes in situations where there is also a high demand for steam and/or power. This is the case for SAGD projects where the steam demand can be balanced with the OrCrude Process design and operation. Because of the high energy export, an OrCrude based Upgrader is not as applicable for an Athabasca

bitumen mining project. The high production of excess energy from an OrCrude based plant results in a relatively low SCO yield (80-83 V %). The Upgrader investment is fairly high primarily a result of the large expensive gasification unit. There are concerns regarding the selection of DAO thermal cracking as the third step in the process and the recycling of thermally cracked liquids to the crude fractionation; however OPTI Canada has addressed these issues in the Cold Lake demonstration plant. It is important to note that the thermal cracking of SDA DAO can result in additional asphaltene production which will increase the rate of asphaltenes from the SDA and to the gasifier. This will decrease the overall SCO liquid yield. Another concern is that OPTI developed their own SDA process utilizing a world expert in the field rather than using available licensable

Product & Waste Issues: The Long Lake Project will produce a 39°API SCO and there are no issues with this product. Wastes include spent catalyst and gasifier soot, neither presents any large issues.

technologies from Axens, UOP or KBR.

Scale-up: The scale-up from the 1 BPD pilot plant in Israel to a demonstration facility (500 BPD) in Cold Lake, Canada was successful. The scale-up from the demonstration facility to the commercial size (76,000 BPSD Long Lake Project) should not have been difficult.

Patents: OPTI Canada has been very active in the development of patents concerning the overall processing scheme (distillation/SDA/thermal cracking) and those covering the SDA step, which was developed by OPTI. The patents are well written but since the processing steps are well known technologies, a small amount of new technical knowledge is contained in the patents.

R&D Facilities: Beginning in 2001, OPTI Canada operated a 500 BPD pilot unit (cost = \$15 MM) located in Cold Lake., Alberta This facility did not include the downstream hydrocracking and asphaltene gasification steps which are included in the Long Lake Project. The plant has processed over 100,000 Bbl of heavy crude and resulted in optimizing the process and providing a basis for the Long Lake design. The demonstration plant has been shut down.

Current Status: OPTI Canada is currently focused on completing the start-up and ramping-up of feedstock capacity of the Long Lake Project. Although the OrCrude Process is available for license, they are not overly active in marketing the technology at this time. The only significant effort is the Long Lake Project whose status is summarized below:

1. Long Lake Project – Construction of the 72,000 BPSD commercial plant (Phase 1) was completed in 2008 and commissioning and start-up activities were ongoing in 2008. The first quantity of premium SCO was produced in January 2009 with a production rate of 10 - 15,000 BPSD. In 2009, bitumen production and resulting SCO production has been limited by issues concerning the water treatment plant. The gross bitumen feedrate has been limited to 14–18,000 BPSD. Current (May 2010) production is approximately 18,000 BPD of bitumen. There have also been issues with the SAGD steam-to-oil ratio which has averaged 4-5 relative to a long-term expected value of 3.0. Opti/Nexen expects full production by late 2010. Asphaltenes were fed to the gasifier in late 2009 and are gradually phasing out the straight run vacuum residue previously routed to the gasifier.

The plant processes SAGD Athabasca bitumen and is designed to produce 58,500 BPSD (81 V% yield on crude) of a 39°API SCO. After selling a portion of the project ownership to Nexen, Opti is currently a 35% owner of the project. Front end engineering for Phase 2 (same size

as Phase 1) of the project has been completed; however it is currently on-hold.

Strengths / **Weaknesses** / **Unknowns:** A subjective table summarizing the strengths, weaknesses and unknown factors of the OPTI OrCrude Process is shown below.

Strengths	Weaknesses	<u>Unknowns</u>
No Natural Gas Required	Newcomer to Upgrading	Final Energy Balance
Numerous Patents	Low SCO Yield	Final Capital Cost
Good Data from Demo Plant	Expensive Gasification Step	Gasifier Operation with Asphaltene Feedstock
Commercial Long Lake	Use of Own SDA instead of	Future Natural Gas Pricing vs.
Project	Licensed Technology	Gasifier Investment
Designed for SAGD Feed	Limited Feedstock Applicability	
Affiliation with Nexen	Start-up Issues at Long Lake	

The strongest strengths are the current operating commercial plant with a design based on a large demonstration facility, the excellent patent protection, and the fit with a SAGD Project. The strongest weaknesses are the low SCO yield, high investment (primarily the gasification step) and the applicability to SAGD feeds only.

Best Applications: Given the high energy export, the OrCrude Process target market is for Athabasca SAGD feedstocks or other heavy crudes requiring steam or syngas for resource production. The process produces a SCO that does contain any residue and is thus a full upgrading application.

Summary: The OrCrude Process could be a major player in the future upgrading area if the Long Lake Project is completely started-up and the operation and

performance is near design. However, with a relatively low SCO liquid yield and expensive gasification required, high natural gas prices would be a necessary factor for additional implementation in North America.

Uniflex Process

by UOP

Go To: Publications Patents

Process Name: Uniflex Process

Process Type: Slurry-Bed Hydrogen Addition

Company: UOP

U.S. Public Company

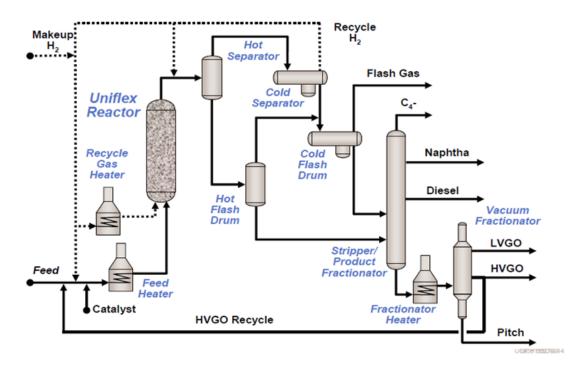
Website: http://www.uop.com

Process Overview & Objective: The UOP Uniflex Process is a slurry hydrocracking technology which was adopted from the CANMET Hydrocracking Process. The CANMET Process was originally developed in the late 1970's and 1980's and is owned by Natural Resources Canada (NRC). CANMET stands for Canadian Centre for Minerals and Energy Technology. Petro-Canada obtained the licensing rights to the CANMET Process in 1979. The process was demonstrated in a 5,000 BPD unit but was never commercialized. In the 1990's, Petro-Canada teamed up with Unocal (now owned by UOP) to offer a CANMET Process with integrated hydrotreating. The new combined process was called U-CAN and involved in-line hydrotreating of the CANMET separator overhead vapor. The U-CAN Process was never commercialized.

UOP obtained exclusive licensing rights to the CANMET Process in 2007. They advanced the technology though R&D and their process technology expertise, and renamed the new process Uniflex. The process claims high conversion (+90%) of the feedstock vacuum residue although lower conversions are possible with the unconverted residue (pitch) sent to a coker or a gasifier. It is a full upgrading process with no vacuum residue in the final SCO product. Since 2008, UOP has been developing the final process with extensive R&D, some of which was funded by the AERI (Alberta Energy Research Institute). In 2008-2009, UOP developed several patent applications for the new process with most of the inventions addressing the slurry additive and the integration of the process with an FCC Unit.

The current Uniflex Process utilizes an iron-based slurry additive which was also the element utilized by the CANMET Process. CANMET used an iron sulfate additive (FeSO₄), where as the Uniflex Process has found that iron-containing bauxite is a preferred additive. The specific or preferred bauxite contains iron oxide (Fe₂O₃) at 10-35 W% and alumina (Al₂O₃) at 55-80 W%. In both processes, the original iron compound converts (100% conversion) to iron sulfide (FeS) which is the active form of the catalyst in the hydrocracking reactor. The reaction of iron oxide to iron sulfide is accomplished at low temperature in the presence of a hydrocarbon, sulfur and hydrogen. The iron crystals formed have sizes of less than 50 nm. UOP claims that the alumina also aids in the Uniflex Process performance (HDS, HDM, etc.). The bauxite additive has a preferred size of approximately 250-550 microns, is not sensitive to the presence of water.

A typical process flow diagram for the Uniflex Process is shown below. The flow scheme and equipment are identical to that utilized for fixed-bed, ebullated-bed or entrained-bed hydrocracking processes. The diagram shows the slurry catalyst



introduced upstream of the fired heater although a UOP patent application states that feeding the slurry downstream of the heater is preferred to avoid sintering or agglomeration of the iron particles. UOP states that an upflow entrained-bed reactor is preferred. The reactor operates at 1,500-2,500 psi, a temperature of 830-870°F and a space velocity of 0.3-1.0 hr⁻¹. The reactor has no internals besides a grid plate distributor. There is no internal recycle via ebullating pumps although UOP states that the reactor accomplishes a high degree of back mixing through optimized operating conditions. An antifoam additive (silicone) is added near the top of the reactor to reduce gas hold-up. VGO is recycled to the reactor at a rate of 5-50% of the feed. This recycle is a critical aspect of the process. The optional external recycle (5-15% of feed) of the vacuum residue product, including the active slurry catalyst is not shown in the diagram.

The reactor effluent is separated in a hot, high pressure separator with the liquid product depressurized and separated into final products via atmospheric and vacuum stills. The cutpoint of the vacuum still bottoms is stated as approximately 840°F in the UOP patent applications. These bottoms can be recycled to increase the vacuum residue (high conversion) and slurry catalyst (higher process performance) in the Uniflex reactor. The net vacuum residue product will contain a high concentration of solids and can be gasified, coked or combusted.

The vapor from the hot high pressure separator is cooled with liquid recovery and separation of water. The vapor from the cold separator is sent to hydrogen recovery (not shown in figure) and net light gas gases reported as product. Optionally the hot separator vapor, which contains significant unreacted hydrogen, can be sent to a vapor or mixed phase hydrotreater or hydrocracker to upgrade or hydrocrack the naphtha, diesel and lighter VGO product. This integrated hydrotreating feature was also included in the CANMET Process.

Claims: The CANMET Process and the Veba Combi-Cracking (VCC) Process were the first slurry catalyst processes and were introduced in the late 1970's. The CANMET Process was considered highly thermal (high temperature) and utilized additives with low catalytic activity but which provided a surface for removal of metals and toluene insoluble material thus allowing high conversion. The process (as well as VCC) was not commercialized as a result of high investment cost, high required additive rates and high hydrogen consumption. The high hydrogen consumption is a necessary result of the high conversion operation but also low hydrogen efficiency due to high light gas yields which consume significant hydrogen. The disposition of the heavy, high solids content vacuum residue was also an important issue. The key CANMET Process claims included:

- 1. The use of iron sulfate as a slurry additive, coal was also investigate as an additive along with the iron, additive rate was up to 4 W% of the feed and ground to a small average size (<50 micron).
- 2. The recycle of VGO and vacuum residue to the slurry reactor.
- 3. High pressure integrated hydrotreating of the hot separator overhead material.
- 4. Attainment of high conversion (>90%) at very high reactor temperature and fairly high LHSV highly thermal process.

Relative to the CANMET Process as available in the 2000-2005 timeframe, UOP has concentrated on the following enhancements:

- 1. The use of water resistant and inexpensive iron-containing bauxite as a catalyst.
- 2. Optimization of catalyst size (250-550 microns) and reactor operating conditions to increase reactor liquid and catalyst backmixing. This will result in a higher iron concentration in the reactor and reduction in

- additive usage. UOP states that there is an "efficient utilization of the rector volume".
- 3. Understanding of mesophase creation and its control to reduce additive consumption and attain long run times
- 4. Enhancement of the integrated hydrotreatment of the VRSH distillates and VGO using UOP fixed-bed expertise.
- 5. Integration of the process with an FCC Unit including recycle of cycle oils
- 6. Applications at moderate conversion with the unconverted residue routed to a coker or gasifier. This would be competitive with the existing ebullated-bed technologies, H-Oil and LC-Fining.

The major UOP enhancements to the CANMET Process are the bauxite additive and the improved utilization of the reactor via optimized operating conditions. Typically entrained reactors are plug flow and require hydrogen injection along the reactor to reduce the temperature increase due to the exothermic reactions. UOP reports that the reactor is near isothermal due to intense backmixing. It is not clear how this is attained although the additive particle size, antifoam additive and external recycles are important aspects.

The additive is preferably added downstream of the feed fired heater or directly into the reactors. Additional catalyst is fed via a recycle of a heavy vacuum residue recycle stream. The additive rate is such to attain approximately 0.4 to 1.5 W% iron in the Uniflex reactor. With 15% vacuum bottoms recycle and assuming 1 W% iron in the reactor and 25% iron oxide in bauxite as a basis, it is estimated that 4 W% bauxite addition is required in the heavy oil feedstock. The market cost of commodity bauxite (late 2009) is approximately \$125/ton. The estimated catalyst cost (not revealed by UOP) is therefore \$0.90 per Bbl of feed. This is significantly lower than that for ebullated-bed systems (\$2-3/Bbl) which however, produce a more highly upgraded product.

Although attaining nearly 100 percent conversion is seemingly desirable, it requires a very high initial investment and operating cost which may not be economically justified. As vacuum residue conversion increases, there is a higher selectivity to undesirable light gas products which contain high hydrogen contents. High conversion (>90%) will consume approximately 2,000 SCF per Bbl of feedstock, not including secondary hydrotreatment. At a high \$8/1000 SCF of natural gas cost, this hydrogen consumption will correspond to an operating cost of over \$8/Bbl of feedstock.

Product & Waste Issues: The spent slurry catalyst is removed with the heavy liquid product (vacuum tower bottoms or pitch) and will be at a high concentration particularly at the high conversion levels expected. For example, at 90% conversion, the heavy liquid will contain 9 times the concentration of catalyst that was added in the feed. The disposal of this purge stream may be difficult. Gasification, coking, and combustion of the bottoms are possible outlets for the bottoms product. UOP is also developing a pitch solidification step so that the material can be easily transported.

The distillate products from the process will be of relatively poor quality compared to products from the more catalytic ebullated-bed or fixed-bed processes. The Uniflex distillates will require more severity hydrotreating; this is probably a reason for the development of the integrated hydrotreating feature which takes advantage of the available high hydrogen partial pressure.

Scale-up: The scale of the UOP and NCUT Uniflex pilot units is unknown but probably in the range of 5–20 gal/hr. UOP claims that the process was scaled-up via the CANMET 5,000 BPD demonstration plant at Petro-Canada's Montreal

refinery. This unit demonstrated long-term operations including the establishment of equilibrium recycle quality. A new demonstration or large-scale pilot unit has not been announced by UOP.

The new technology features included with the Uniflex Process include the new additive (bauxite) and size, integrated hydrotreatment and optimized operating conditions including recycle type and rates. Additional demonstration of the process in a large unit to assess scale-up of these items is judged to be unnecessary. UOP also claims high level of reactor backmixing in the entrained reactor. If this claim is critical to enhanced process performance and involves reduced gas and liquid velocities or reduction in gas hold-up, it may require scale-up confirmation. This could be accomplished in an inexpensive cold model.

Patents: No patents have been granted to UOP for the Uniflex Process although ten U.S. patent applications were filed in 2009. All the patent applications are similar in content and have similar claims. UOP's strategy is unclear with the filing of these similar applications and it is doubtful if more than two would be granted. The important technical revelations in the UOP applications are the use of iron-containing bauxite as the feed additive, the additive particle size (250–554 micron), and the integration with an FCC Unit. Additionally, UOP includes an in depth discussion of the detection, classification of and minimization of coke and mesophase (coke precursors) though electron microscopy and x-ray diffraction. Two of the UOP applications concern the integration with an FCC Unit with recycle of the FCC heavy slurry or decant oil to the Uniflex reactor.

A large subset (seventeen) of the issued U.S. patents for the CANMET Process is included in Attachment 2. These were issued to NRC or its predecessors and Petro-Canada. The issued U.S. patents cover many aspects of the technology as it

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evolved from 1978 through 2003. This includes including catalyst preparation,

different additives and particle sizes, integrated hydrotreating, VGO and residue

recycles, and use of anti-foam. Many of the patents have expired.

R&D Facilities: UOP has constructed a new pilot plant to support the

development of the Uniflex Process. The pilot plant scale and feed capacity are

unknown. UOP executed a \$1.4 MM contract with NRC for pilot plant support

while the UOP unit was under design/construction. A pilot unit (size unknown)

was operated at the NCUT laboratory in Edmonton as part of the Alberta Energy

Research Institute HUPD (Hydrocarbon Upgrading Demonstration Program).

This was funded, in part by the Alberta government and appears to have

concentrated on new slurry additive testing and the development of the integrated

hydrotreating aspect of the technology.

The UOP patent applications utilized a small semi-continuous pilot facility which

processed approximately 3 gal/day of feedstock. An NRC reference in

Attachment 1 also mentions that a Uniflex Process pilot plant was operated by

Statoil Hydro (now Statoil ASA). The Statoil reference may be in relation to the

Kai Kos Dehseh Project (formerly North American Oil Sands Project) which was

originally a coker-based upgrader. Given the capabilities and expertise of UOP, it

is clear that that they have sufficient R&D facilities and know-how to fully

develop and optimize the process.

The CANMET Process was developed by NRC in pilot units and demonstrated in

the 5,000 BPD plant in Petro-Canada's Montreal refinery. The demonstration unit

has been shutdown and is presumably now longer available for studies.

Current Status: UOP has been developing the Uniflex process since 2007 with

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financial assistance from the Alberta government. In addition to the AERI program, the recent UOP emphasis has been on the construction and initial operation of the pilot plant, development of patent application and marketing/technical publications. The only possible application found was the mention of a Uniflex pilot plant at Statoil which is the owner of the former North American Oil Sands Project in Alberta.

Strengths / Weaknesses / Unknowns: The table on the following page is a preliminary assessment of the strengths and weaknesses of the UOP Uniflex Process.

Strengths	Weaknesses	<u>Unknowns</u>	
UOP Licensed	Latecomer to Slurry	Performance Relative to HCAT,	
	Hydrocracking	EST, HRH,VRSH	
CANMET Process Data &	Unconverted Residue has no	Net Catalyst Cost	
History	Utility/Value		
Operating Pilot Plant	Catalyst Recycle Required	Economics Relative to	
		Ebullated-Bed	
Emphasis on High	High Pressure - High	Degree of Reactor Backmixing	
Conversion	Investment	and how Attained	
Prior Demo Plant	High H ₂ Usage – High	Role of Antifoam and Effect of	
Operation	Operating Costs	New Uniflex Additive	
High Level of Technical	Possible Fouling in		
Expertise - Asphaltenes	Downstream Vessels		
Bauxite Additive			

The largest strengths are the licensor UOP who is a major refining technology licensor with access to projects worldwide and the bauxite additive which appears to be inexpensive and provides good performance in terms of attaining high conversion with minimal fouling. Major weaknesses include that there are already several (>6) slurry catalyst processes, none of which have currently been commercialized and the estimated high investment and operating costs (H₂) which

are characteristic of all slurry catalyst technologies. Significant unknowns are the process performance relative to other slurry catalyst processes and the process economics relative to commercial residue hydrocracking technologies.

Best Applications: The Uniflex Process is a full upgrading process and is being developed for moderate to high residue conversion. UOP appears to be specifically targeting Canadian bitumen and heavy oil applications. Given the very high hydrogen usage, it may be best applicable for regions with low natural gas cost. For Western Canada, a lower conversion version of the process may be more applicable with the unconverted residue used for coker or gasifier feed.

Summary: The Uniflex Process is one of the many high conversion slurry catalyst processes, none of which have been commercialized although a commercial EST plant is currently under construction. The use of bauxite as the catalyst additive may have advantage over the existing similar technologies. The application of slurry catalyst technology at very high conversion (>90%) is typically not technical or economically attractive as a result of high hydrogen consumption, high investment cost and the extremely poor quality of the unconverted residue. Application at milder conditions (75-80% conversion) with the unconverted residue routed to a gasifier or coker may be the preferred configuration and would have a greater potential for eventual commercialization. As with the Chevron VRSH process, the Uniflex Process is puzzling given the similar full developed processes which have not been commercialized. Given that UOP is the world's largest refining technology licensor, the Uniflex Process has a high probability of eventual commercialization.

Vacuum Resid Slurry Hydrocracking

(VRSH) Process

by Chevron

Go To: Publications Patents

Process Name: Vacuum Resid Slurry Hydrocracking (VRSH) Process

Process Type: Slurry-Bed Hydrogen Addition

Company: Chevron Company

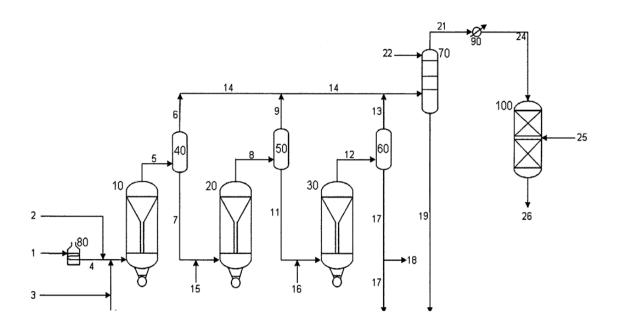
U.S. Public Company

Website: http://www.chevron.com

Process Overview & Objective: The Chevron Vacuum Resid Slurry Hydrocracking (VRSH) Process is a new slurry catalyst process which was piloted in California and has announced plans for a demonstration plant in Mississippi. The process claims nearly 100 percent conversion of the feedstock vacuum residue. It is considered to be a full upgrading process with no vacuum residue in the final SCO product. The 3,500 BPD VRSH demonstration plant was planned for construction in 2008 but has been delayed until at least 2010. Chevron has been developing the process since 2003 and in the 2005-2008 timeframe developed a comprehensive patent portfolio (26 patents and applications) concerning many aspects of the process.

The VRSH process utilizes a molybdenum-based slurry additive with a nickel promoter (provides high sulfur and nitrogen removal) and recycle of the catalyst via a heavy liquid recycle stream. The catalyst is micron-size or larger and the required concentration in the reactor is fairly high. To be economical, the commercial process will require the catalyst recovery and recycle steps. Many of the Chevron patent and patent applications concern the preparation of the active catalyst which involves numerous steps at moderate temperature and pressure. The catalyst preparation technology is similar to that used for the Headwaters HCAT Process.

A typical process flow diagram for the VRSH Process is shown below. The catalyst is introduced with the preheated feed and enters the well-mixed reactors. Chevron specifies a series of well-mixed or ebullated-beds for the VRSH Process. The reactors, as described in the patents and patent applications, typically have



internal recycle (ebullating pumps at the bottom of the reactor) which accomplishes the well-mixed bed and distributes the catalyst slurry uniformly. The internal reactor recycle requires a separation device located in VRSH Reactor. The external recycle of the heavy product, including the still active slurry catalyst is not shown in the diagram.

Chevron includes numerous processing options in their patent and patent applications including:

- 1. The use of two or more reactor stages in series
- 2. Interstage separation to reduce feedrate to the subsequent VRSH reactor stage

3. Elimination of the interstage separators and draw off of liquid from the internal reactor separators as feed to the subsequent stage (vapor is product)

4. In-line or integrated hydrotreatment of the VRSH distillates and VGO

5. Feed of heavy oil feedstock or lighter feeds (e.g. VGO) in-between reactor stages

In all cases, very high conversion of the feedstock vacuum residue is claimed with only a small bleed stream of unconverted residue and slurry catalyst.

Claims: The major claim is that the high activity of the catalyst results in improved hydrogenation and cracking reactions in the VRSH Reactors such that the reactor operating conditions can be reduced relative to existing slurry processes. Additionally, Chevron claims that the possibility of catalyst agglomeration and associated poor operating time is minimized. Relative to the fixed-bed and ebullated-bed processes, the VRSH Process can more readily attain higher levels of residue conversion, with higher liquid yields (i.e., more SCO) in a commercial upgrader.

Although attaining nearly 100 percent conversion is seemingly desirable, it requires a very high initial investment and operating cost which may not be economically justified. As vacuum residue conversion increases, there is a higher selectivity to undesirable light gas products which contain high hydrogen contents. High conversion (>90%) will consume approximately 2,000 SCF per Bbl of feedstock, not including secondary hydrotreatment. At a high \$8/1000 SCF of natural gas cost, this hydrogen consumption will correspond to an operating cost of over \$8/Bbl of feedstock.

Additionally, internal process streams in a commercial VRSH plant will contain converted distillates and VGO as well as unconverted vacuum residue. As the

conversion is increased, these internal streams will become very unstable

(incompatible) and have a propensity to produce sediment and eventual process

shutdowns. The demonstration plant planned by Chevron may have included

design features to minimize this problem, however it is expected that long-term

stable operation may be difficult at the high residue conversion levels touted by

Chevron.

Product & Waste Issues: The spent slurry catalyst is removed with the heavy

liquid product and will be at a high concentration particularly at the high

conversion levels expected. For example, at 90% conversion, the heavy liquid

will contain 9 times the concentration of catalyst that was added in the feed. The

disposition of this purge stream will be difficult. Gasification or combustion of

the bottoms will help to alleviate this issue since the catalyst is removed in the

gasifier.

Scale-up: Chevron is planning a 3,500 BPD VRSH demonstration plant to fully

scale-up the process. Long-term operation (sediment issue at high conversion

levels), reactor internals demonstration, and establishing equilibrium catalyst

recycle will be key features in the demonstration plant. Chevron must have judged

that there was a need to address process scale-up given the large investment for the

demonstration plant.

Patents: As of late 2009, Chevron has been granted twelve U.S. patents on the

VRSH and has filed fourteen additional patent applications. The issued U.S.

patents cover all aspects of the technology including catalyst preparation, reactor

design, catalyst recycle and reactor processing configurations, including in-line

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hydrotreating. The patent applications concern additional variations of the catalyst

preparation, reactor internals, process configurations, and concepts for custom

SCO preparation. The patents and patent applications are the primary source of

current information concerning the VRSH Process.

R&D Facilities: Chevron has sufficient R&D facilities and know-how to fully

develop and optimize the process and to perform feedstock and catalyst

evaluations. The VRSH Process pilot plant was located in California and is still

operable. The planned demonstration plant (3,500 BPD) will be located in the

Chevron Pascagoula Mississippi refinery and will presumably contain all of the

features of a commercial VRSH Process facility. As of mid 2010, there is no

available update on the demonstration plant schedule.

Current Status: Previously, the process was being developed with a good deal of

secrecy. In the past year few years there have been two Chevron press releases

and a great deal of effort on the development of intellectual property. Although

detailed information is unavailable, the recent emphasis must have been on the

operation of the pilot plant and the design of the 3,500 BPD demonstration

facility.

Strengths / Weaknesses / Unknowns: The table on the following page is a

preliminary assessment of the strengths and weaknesses of the Chevron VRSH

Process.

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Strengths	Weaknesses	<u>Unknowns</u>
Chevron Developed Latecomer to Slurry Hydro	Latecomer to Slurry Hydrocracking	Performance Relative to
		HCAT, EST, HRH
Proper Development	Unconverted Residue has no Utility	Real Catalyst Cost
Strategy	Onconverted Residue has no Othity	
Operating Pilot Plant	Catalyst Recycle Required	Economics Relative to
		Ebullated-Bed
Emphasis on High	High Pressure, High H ₂ Usage (High	
Conversion	Investment and Operating Costs)	
Demo Plant Planned	Emphasis on Very High Conversion	
	Fouling in Downstream Vessels	

The largest strength of the VRSH Process is its developer Chevron who is a major refining technology licensor with access to world-class pilot and demonstration facilities. Major weaknesses include that there are already several (>6) slurry catalyst processes, none of which have currently been commercialized. Chevron's late entry into slurry hydrocracking is puzzling and may indicate that they have an unknown advantage or breakthrough. The greatest weaknesses are the high catalyst usage rate (requiring recovery and recycle) and the estimated high operating cost and investment.

Best Applications: The VRSH Process is a full upgrading process and is being developed for near 100 percent residue conversion. Given the very high hydrogen usage, it may be best applicable for regions with low natural gas cost. For Western Canada, a lower conversion version of the process may be more applicable with the unconverted residue used for gasifier feed (hydrogen and/or power production).

Summary: The VRSH Process is one of the many high conversion slurry catalyst processes, none of which have been commercialized although a commercial EST plant is currently under construction. The application of slurry catalyst technology

at very high conversion (>90%) is typically not technical or economically attractive as a result of high hydrogen consumption, high investment cost and the extremely poor quality of the unconverted residue. Application at milder conditions (75-80% conversion) with the unconverted residue routed to a gasifier may be the preferred configuration and would have a greater potential for eventual commercialization. The VRSH Process remains a puzzle given the similar processes which have not been commercialized and the 2009 postponement of the demonstration plant.

Attachment 1

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Return To: Process Write-Up

Partial Upgrading Processes

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- **e.** Gillis, D., et al, "*Upgrading Residues to Maximize Distillate Yields*", Presented at the NPRA Annual Meeting, San Antonio, TX, March 22-24, 2009.
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- **g.** "CANMET Residuum Hydrocracking: Advances through Control of Polar Aromatic", Petro-Canada, Presented at the 1996 NPRA Annual Meeting, San Antonio, TX, March 1996.

- **h.** "The CANMET Hydrocracking Process: Recent Developments", Petro-Canada, SNC Lavalin and Unocal, Presented at the Oil Sands our Petroleum Future Conference, Edmonton, AB, Canada, April 1993.
- i. "CANMET Hydrocracking Process for Heavy Oil Upgrading", Partec Lavalin, Presented at the 8th CHEMTECH Conference, New Delhi, India, October 1990.
- j. "Demonstration of the High Conversion CANMET Hydrocracking Process on Cold Lake Vacuum Residue", Presented at the Oilsands 2000 Conference, March 1990.
- **k.** "Upgrading of Cold Lake Heavy Oil in the CANMET Hydrocracking Demonstration Plant", Petro-Canada, Presented at the Fourth International Conference on Heavy Crudes, Edmonton, AB, Canada, August 1988.
- "The CANMET Hydrocracking Process Upgrading of Cold Lake Heavy Oil", Petro-Canada, Published in Chemistry in Canada, March 1981.

News Articles

a. Diesel Fuel News, "Uniflex Hydrocracking Beats Coking Hands-Down on Boosting Distillate: UOP", 2009.

8. Vacuum Resid Slurry Hydrocracking (VRSH) by Chevron

Publications

a. Successful Commercialization of Heavy Oil: The ChevronTexaco Experience", ChevronTexaco, Presented at the Heavy Oil Forum, Puerto La Cruz, October, 2003. (Available from Colyar Consultants)

News Articles

- **b.** Reuters News Service, "Chevron to Delay Miss. Refinery Pilot Project", February 5, 2009.
- c. Chevron News Release, "Chevron Unveils New Refining Technology that Converts Ultra-Heavy Oil into Clean-Burning Fuel", March 6, 2008.

Attachment 2

Listing of Important Patents and Applications

Partial Upgrading Processes

1. Aquaconversion by Foster Wheeler and UOP

- **a.** U.S. Patent 5,688,741 "*Process and Catalyst for Upgrading Heavy Hydrocarbon*", Inventors: Pereira P., Martinez N., and Carrazza J., Assignee: Intevep S.A., Filed: March 17, 1995, Granted: November 18, 1997.
- **b.** U.S. Patent 5,885,411, "*Steam Conversion Process and Catalyst*", Inventors: Pereira P., Marzin R., Zacarias L., Carrazza J., and Marino M., Assignee: Intevep S.A., Filed: April 11, 1997, Granted: March 23, 1997.

2. Catalytic Crude Upgrading (CCU) Process by UOP

- **a.** U.S. Patent Application 2007/0034550, "*Process and Apparatus for Improving Flow Properties of Crude Petroleum*", Inventors: Hedrick, B, McGhee, J., Erisken, A. and Qafisheh, J. (UOP), Filed: August 9, 2005, Published: February 15, 2007.
- **b.** U.S. Patent 4,992,160, "Conversion of Crude Oil Feeds by Catalytic Cracking", Inventors: Long, G., Pellet, R. and Rabo, J., Filed: April 10, 1987, Granted: February 12, 1991.
- **c.** U.S. Patent 4,976,846, "*Conversion of Crude Oil Feeds*", Inventors: Long, G., Pellet, R. and Rabo, J., Filed: February 2, 1989, Granted: December 11, 1990.
- **d.** U.S. Patent 4,803,184, "*Conversion of Crude Oil Feeds*", Inventors: Long, G., Pellet, R. and Rabo, J., Filed: November 27, 1984, Granted: February 7, 1989.

3. CPJ Process by Wesco Energy Corp.

a. U.S. Patent 6,989,091, "Deep Conversion Combining the Demetalization and the Conversion of Crudes, Residues, or Heavy Oils into Light Liquids with Pure or Impure Oxygenated Compounds", Inventor: Jorgensen, P., Filed: May 2, 2003, Granted: January 24, 2006.

4. EADIEMAC Process by Eadie Oil Inc.

a. U.S. Patent 5,110,447, "*Process and Apparatus for Partial Upgrading of a Heavy Oil Feedstock*", Inventors: MacWilliams, W. and Eadie, W., Filed: September 12, 1988, Granted: May 5, 1992.

5. Heavy to Light Oil (HTL) Process by Ivanhoe Energy Inc.

- **a.** U.S. Patent Application 20090266380 "Mitigation of Deposits and Secondary Reactions In Thermal Conversion Processes", Inventors: Freel, B. and Hopkins, G., Filed: October 29, 2009.
- **b.** U.S. Patent 7,572,365 "Modified Thermal Processing Of Heavy Hydrocarbons Feedstocks", Inventors: Freel and Clarke, D., Filed: October 11, 2002, Granted: August 20, 2009.
- **c.** U.S. Patent 7,572,362 "Modified Thermal Processing Of Heavy Hydrocarbons Feedstocks", Inventors: Freel, B., Kriz, J. and Clarke, D., Filed: April 11, 2003, Granted: August 11, 2009.
- **d.** U.S. Patent Application 20080230440 "Methods and Systems for Producing Reduced Resid and Bottomless Products from Heavy Hydrocarbon Feedstocks", Inventors: Freel, B. and Graham, R., Filed: March 11, 2008.
- e. U.S. Patent 7,270,743, "Products Produced from Rapid Thermal Processing of Heavy Hydrocarbon Feedstocks", Inventors: Freel, B. and Graham, R., Filed September 18, 2001, Granted: September 18, 2007.
- **f.** U.S. Patent 5,961,786 "Apparatus for a Circulating Bed Transport Fast Pyrolysis Reactor System", Inventors: Freel, B. and Graham, R., Assignee: Ensyn Technologies, Inc., Filed: June 15, 1998, Granted: October 5, 1999.
- **g.** U.S. Patent 5,792,340, "*Method and Apparatus for a Circulating Bed Transport Fast Pyrolysis Reactor System*", Inventors: Freel, B. and Graham, R., Assignee: Ensyn Technologies, Inc., Filed: April 7, 1995, Granted: August 11, 1998.
- **h.** Canadian Patent Application 2369288 "*Rapid Thermal Processing Of Heavy Hydrocarbons Feedstocks*", Inventor: Graham, R., Filed: 2002.

6. H-Oil Process by Axens North America

a. No U.S. or Canadian Patents or Patent Applications Relating to Partial Upgrading Found

7. I^YQ Process by ETX Systems Inc.

- **a.** Canadian Patent 2,505,632, "A Process for Converting a Liquid Feed Material into a Vapor Phase Product", Inventors: Brown, W.A., Monaghan, G.A. and Pinchuk, R.J., W., Filed: October 26, 2004, Granted: September 5, 2006.
- **b.** U.S. Patent Application 20050279671, "A Process for Converting a Liquid Feed Material into a Vapor Phase Product", Inventors: Brown, W.A., Monaghan, G.A. and Pinchuk, R.J., W., Filed: December 22, 2005.

8. Jet Shear Process by Fractal Systems Inc.

- **a.** U.S. Patent Application 20080314796, "*Treated Oils having Reduced Densities and Viscosities*", Inventors: Chornet, E. and Chornet, M., Filed: December 25, 2008.
- **b.** U.S. Patent Application 20080217211, "*Process for Treating Heavy Oils*", Inventors: Chornet, E. and Chornet, M., Filed: September 11, 2008.
- **c.** U.S. Patent 5,096,566, "*Process for Reducing the Viscosity of Heavy Hydrocarbon Oils*", Inventors: Dawson, B., Chornet, E., Overend, R., Amitabha, C. and Lemonnier, J., Filed: February 11, 1991, Granted: March 17, 1992.

9. PetroBeam Process by PetroBeam, Inc.

a. U.S. Patent Application 20100051444 "*Self-Sustaining Cracking of Hydrocarbons*", Inventors: Zaikin, Y. and Zaikina, R., Filed December 15, 2006, Published March 4, 2010.

10.PetroSonic Heavy Oil Upgrader by SONIC Technology Solutions Inc.

- **a.** Patent Application WO 2009/111,871, "*Method for Treating Heavy Oil Crude*", Inventors: Hill, J. and Arato, C., Assigned to Sonic Technology Solutions, Filed: March 11, 2009, Published: September 17, 2009.
- **b.** U.S. Patent Application 2007/0267327, "*Heavy Oil Upgrading Process*", Inventor: Boakye, F., Filed: March 23, 2007, Published: November 2, 2007.
- **c.** U.S. Patent Application 2006/0094922, "Sonication Treatment of Media Containing Halogenated Organic Compounds", Inventors: Hunt, L., McKinley, J. and McElroy, R., Filed: October 23, 2005, Published: May 4, 2006.

d. U.S. Patent 6,984,767, "Sonication Treatment of Polychlorinated Biphenyl Contaminated Media", Inventors: Hunt, L., McKinley, J. and McElroy, R., Filed: April 23, 2003, Granted: January 10, 2006.

11.Sonocracking[™] by SulphCo

- **a.** U.S. Patent 7,559,241, "*High-Throughput Continuous-Flow Ultrasound Reactor*", Inventor: Gunnerman R, Filed: May 27, 2004, Granted: July 14, 2009.
- **b.** U.S. Patent 7,408,290, "*Power Driving Circuit for Controlling a Variable Load Ultrasound Transducer*", Inventors: May, J.., Richman, R. and Gunnerman R, Filed: February 28, 2005, Granted: August 5, 2008.
- c. U.S. Patent 7,300,566, "Conversion of Petroleum Resid to Usable Oils with Ultrasound", Inventor: Gunnerman R., Assignee: SulphCo, Inc., Filed: March 1, 2004, Granted: November 27, 2007.
- **d.** U.S. Patent 7,275,440, "Loop-Shaped Ultrasound Generator and its Use in Chemical Reactions", Inventors: Gunnerman R. and Richman R., Assignee: SulphCo, Inc., Filed: November 18, 2004, Granted: October 2, 2007.
- e. U.S. Patent Application 20060260405, "Loop-Shaped Ultrasound Generator and Use in Reaction Systems" Inventors: Gunnerman, R. and Richman, R., Assignee: SulphCo, Inc., Filed: July 14, 2006, Published: November 23, 2006.
- **f.** U.S. Patent Application 20060196915, "*High-Power Ultrasound Horn*", Inventor: Gunnerman R, Filed: February 24, 2005, Published: September 7, 2006.
- **g.** U.S. Patent Application 20060180500, "Upgrading of Petroleum by Combined Ultrasound and Microwave Treatments", Inventor: Gunnerman R, Filed: February 15, 2005, Published: August 17, 2006
- **h.** U.S. Patent 6,897,628, "*High-Power Ultrasound Generator and Use in Chemical Reactions*", Inventors: Gunnerman R. and Richman R., Assignee: SulphCo, Inc., Filed: May 16, 2003, Granted: May 24, 2005.
- i. U.S. Patent 6,827,844, "*Ultrasound-Assisted Desulfurization of Fossil Fuels in the Presence of Di-alkyl Ethers*", Inventors: Gunnerman R., Assignee: SulphCo, Inc., Filed: October 23, 2002, Granted: December 7, 2004.
- **j.** U.S. Patent Application 20030051988, "Treatment of Crude Oil Fractions, Fossil Fuels and Products Thereof with Ultrasound", Inventors: Gunnerman R, Moote P. and Cullen M, Filed: May 22, 2001, Published: March 20, 2003.

- **k.** U.S. Patent 6,652,992, "*Corrosion Resistant Ultrasonic Horn*", Inventors: Gunnerman R., Assignee: SulphCo, Inc., Filed: December 20, 2002, Granted: November 25, 2003.
- **l.** U.S. Patent 6,500,219, "Continuous Process for Oxidative Desulfurization of Fossil Fuel with Ultrasound and Products Thereof", Inventors: Gunnerman R., Assignee: SulphCo, Inc., Filed: March 19, 2001, Granted: December 31, 2002.
- m. U.S. Patent 6,402,939, "Oxidative Desulfurization of Fossil Fuel with Ultrasound", Inventors: Yen T., Mei, H., Lu S., Assignee: SulphCo, Inc., Filed: September 28, 2000, Granted: June 11, 2002.

12.TRU Process by TRU Oiltech

a. WO International Patent Application PCT/CA2007/000599, "*Method of Upgrading Heavy Crude Oil*", Inventors: Constable, G., Carlson, N, Heelan, G. and Oehr, K., Assignee: TRU Oiltech Inc., Filed: April 11, 2007, Published: October 23, 2008.

13. Value Creation Technology by BA Energy

- **a.** U.S. Patent 7,625,466, "System for the Decontamination of Asphaltic Heavy Oil and Bitumen", Inventor: Yeung, C.K., Assignee: Value Creation Inc., Filed: May 16, 2006, Granted: December 1, 2009.
- **b.** U.S. Patent Application 20060260982, "*Pyrolysis of Residual Hydrocarbons*", Inventor: Yeung, C.K., Filed: November 23, 2006.

14.VISCOSITOR by Ellycrack A/S

- **a.** U.S. Patent Application, 20090120844, "*Process for Simultaneous Recovery and Cracking/Upgrading of Oil for Solids*", Inventors: Ellingsen, O. and Ellingsen, B., Filed: May 14, 2009.
- **b.** U.S. Patent Application, 20070193924, "Low Temperature Thermodynamic Cracking and Conversion for Upgrading of Heavy Oils", Inventor: Ellingsen, O., Filed: August 23, 2007.
- **c.** U.S. Patent 6,660,158, "*Catalytic Cracking Process*", Inventor: Ellingsen, O., Filed: February 10, 2000, Granted: December 9, 2003
- **d.** U.S. Patent 6,485,631, "*Process for Thermal, and Optionally Catalytic, Upgrading and Hydrogenation of Hydrocarbons*", Inventor: Ellingsen, O., Filed: January 27, 2000, Granted: November 26, 2002.

e. U.S. Patent 5,914,027, "*Thermo-Mechanical Cracking and Hydrogenation*", Inventor: Ellingsen, O., Filed: March 11, 1997, Granted: June 22, 1999.

15. Wildcatter HCU Process by Refinery Science

- **a.** U.S. Patent Application 20080209797, "*Liquid Fuel Feedstock Production Process*", Inventors: Rendina, D. and Hauptman, E., Filed: September 4, 2008.
- **b.** U.S. Patent 7,223,713, "*Molybdenum Sulfide/Carbide Catalysts*", Inventors: Alonso, G., et al., Assigned to Board of Regents, the University of Texas System, Filed: April 7, 2004, Granted: May 27, 2007.
- **c.** U.S. Patent 7,060,650, "*Hydrogenation Catalysts and Methods*", Inventor: Rendina, D.D., Filed: September 27, 2005 Granted: June 13, 2006.
- **d.** U.S. Patent 7,008,895, "*Method for Producing an Improved Supported Catalyst*", Inventor: Rendina, D.D., Filed: January 4, 2003, Granted: March 7, 2006.
- e. U.S. Patent 6,143,359, "Soluble Metal Hydride/Transition Metal Dichalcogenide Alloys", Inventor: Rendina, D.D., Assigned to Lightyear Technologies Inc., Filed: April 14, 1998, Granted: January 7, 2000.
- f. U.S. Patent 5,932,372, "Composite Materials, Processes for Manufacturing the Composites, Composite Electrode, Hydrogen Occluding Composite, and Electrochemical Cell Utilizing the Composite", Inventor: Rendina, D.D., Assigned to Lightyear Technologies Inc., Filed: January 2, 1997, Granted: August 3, 1999
- **g.** U.S. Patent 4,996,108, "Sheets of Transition Metal Dichalcogenides", Inventors: Divigalpitiya, D.M., et al., Assigned to Simon Fraser University, Filed: January 17, 1989, Granted: February 26, 1991.
- **h.** U.S. Patent 4,853,359, "*Novel Transition Metal Dichalcogenide Catalysts*", Inventors: Morrison, S.R, et al., Assigned to Simon Fraser University, Filed: February 18, 1987, Granted: August 1, 1989.
- i. U.S. Patent 4,822,590, "Forms of Transition Metal Dichalcogenides", Inventors: Morrison, S.R., et al., Assigned to Simon Fraser University, Filed: April 23, 1986, Granted: April 18, 1989.

16.WRITE Process by Western Research Institute

- **a.** U.S. Patent 7,594,978, "Apparatus for Continuous Coking Refining", Inventors: Brecher, L., Johnson, L. and Sethi, V., Assigned to University of Wyoming Research Corporation, Filed: November 1, 2005, Granted: September 29, 2009.
- **b.** U.S. Patent Application 20080093259, "Hydrocarbonaceous Material Processing Methods and Apparatus", Inventor: Brecher, L., Filed: April 24, 2008.

c. U.S. Patent 6,972,085, "*Continuous Coking Refinery Methods and Apparatus*", Inventors: Brecher, L., Johnson, L. and Sethi, V., Assigned to University of Wyoming Research Corporation, Filed: May 24, 2002, Granted: December 6, 2005.

Full Upgrading Processes

1. Chattanooga Process by Chattanooga Corp.

- **a.** U.S. Patent Application 20050252833, "*Process and Apparatus for Converting Oil Shale or Oil Sand (Tar Sand) to Oil*", Inventors: Doyle, J. and Hildebrandt, F., Assigned to Chattanooga Corp., Filed: May 31, 2005, Published: November 17, 2005.
- b. U.S. Patent Application 20050252832, "Process and Apparatus for Converting Oil Shale of Oil Sand (Tar Sand) to Oil", Inventors: Doyle, J. and Hildebrandt, F., Assigned to Chattanooga Corp., Field: May 11, 2005, Published: November 17, 2005.
- **c.** U.S. Patent Application 20020054836, "*Process and Apparatus for Converting Oil Shale of Oil Sands to Oil*", Inventors: Kirkbride, C., Doyle, J. and Hildebrandt, F., Assigned to Chattanooga Corp., Published: May 9, 2002.
- **d.** U.S. Patent 6,319,395, "*Process and Apparatus for Converting Oil Shale or Tar Sands to Oil*", Inventors: Kirkbride, C., Doyle, J. and Hildebrandt, F., Assigned to Chattanooga Corp., Filed: March 9, 2000, Granted: November 20, 2001.
- e. U.S. Patent 6,139,722, "Process and Apparatus for Converting Oil Shale or Tar Sands to Oil", Inventors: Kirkbride, C., Doyle, J. and Hildebrandt, F., Assigned to Chattanooga Corp., Filed: April 10, 1998, Granted: October 31, 2000.
- **f.** U.S. Patent 5,902,554, "Apparatus for Converting Oil Shale or Tar Sands to Oil", Inventors: Kirkbride, C., Doyle, J. and Hildebrandt, F., Assigned to Chattanooga Corp., Filed: April 14, 1997, Granted: May 11, 1999.
- **g.** U.S. Patent 5,681,452, "*Process and Apparatus for Converting Oil Shale or Tar Sands to Oil*", Inventor: Kirkbride, C., Assigned to Kirkbride, C., Filed: October 31, 1995, Granted: October 28, 1997.

2. Genoil Hydroconversion Unit (GHU) Technology by Genoil

- **a.** U.S. Patent 7,510,689, "*Method and Apparatus for Introducing Fluids into a Hydrocracking Reactor*", Inventors: Costinel, P., Assignee: Genoil Inc., Filed: December 21, 2005, Granted: March 31, 2009.
- **b.** U.S. Patent 7,014,756, "*Method and Apparatus for Separating Immiscible Phases with Different Densities*", Inventors: Costinel, P., Filed: April 19, 2004, Granted: March 21, 2006.

c. U.S. Patent 7,001,502, "Process for Treating Crude Oil Using Hydrogen in a Special Unit", Inventors: Satchwell R., et al, Filed: September 29, 1999, Granted: February 21, 2006.

3. Eni Slurry Technology by Eni S.p.A.

- **a.** U.S. Patent 7,691,256, "*Process for the Conversion of Heavy Charges such as Heavy Crude Oils and Distillation Residues*", Inventors: Montanari, R., Marchionna, M., Rosi, S., Panariti, N. and Delbianco, A., Assignee: Eni S.p.A., Snamprogetti S.p.A., Enitecnologie S.p.A., Filed: December 20, 2005, Granted: April 6, 2010.
- b. U.S. Patent 5,932,090, "Process for the Conversion of Heavy Crude Oils and Distillation Residues to Distillates", Inventors: Marchionna, M., Panariti, N. and Delbianco, A., Assignee: Snamprogetti S.p.A., Filed: May 1, 1996, Granted: August 3, 1999.
- **c.** U.S. Patent Application 20090314681, "*Process for the Total Conversion of Heavy Feedstocks to Distillates*", Inventors: Marchionna, M., Meli, S., Patron, L., Delbianco, A. and Panariti, N., Filed: July 27, 2007, Published: December 24, 2009.
- **d.** U.S. Patent Application 20090261016, "*Process for the Total Conversion of Heavy Feedstocks to Distillates*", Inventors: Marchionna, M., Meli, S., Patron, L., Delbianco, A. and Panariti, N., Filed: July 27, 2007, Published: October 22, 2009.
- e. U.S. Patent Application 20090101540, "Process for the Conversion of Heavy Charges such as Heavy Crude Oils and Distillation Residues", Inventors: Marchionna, M., Delbianco, A., Panariti, N., Montanari, R., Rosi, S. and Correra, S., Filed: October 9, 2008, Published: April 23, 2009.
- **f.** U.S. Patent Application 20060272982, "Process for the Conversion of Heavy Charges such as Heavy Crude Oils and Distillation Residues", Inventors: Montanari, R., Marchionna, M., Rosi, S., Panariti, N. and Delbianco, A., Filed: December 20, 2005, Published: December 7, 2006.
- **g.** U.S. Patent Application 20060186021, "Process for the Conversion of Heavy Charges such as Heavy Crude Oils and Distillation Residues", Inventors: Marchionna, M., Delbianco, A., Panariti, N., Montanari, R., Rosi, S. and Correra, S., Filed: April 17, 2006, Published: August 24, 2006.
- **h.** U.S. Patent Application 20060175229, "*Process for the Conversion of Heavy Charges such as Heavy Crude Oils and Distillation Residues*", Inventors: Montanari, R., Marchionna, M., Panariti, N., Delbianco, A. and Rosi, S., Filed: December 12, 2003, Published: August 10, 2006.

- i. U.S. Patent Application 20060163115, "Process for the Conversion of Heavy Charges such as Heavy Crude Oils and Distillation Residues", Inventors: Montanari, R., Marchionna, M., Rosi, S., Panariti, N. and Delbianco, A., Filed: December 12, 2003, Published: July 27, 2006.
- **j.** WO Patent Application PCT/EP2008/004117141830, "Process for the *Hydroconversion of Heavy Oils*", Inventors: Patron, L., Malandrino, A. and Molinari, M., Filed: May 19, 2008, Published: November 27, 2008.
- **k.** U.S. Patent Application 20030089636, "*Process for the Conversion of Heavy Charges such as Heavy Crude Oils and Distillation Residues*", Inventors: Marchionna, M., Delbianco, A., Panariti, N., Montanari, R., Rosi, S. and Correra, S., Filed: July 5, 2002, Published: May 15, 2003.

4. HCAT by Headwaters Heavy Oil

- **a.** U.S. Patent Application 20100051507, "Hydrocarbon-Soluble Molybdenum Catalyst Precursors and Methods for Making Same", Inventors: Wu, Z., Zhou, Z. and Zhou, B., Assignee: Headwaters Technology Innovation, LLC, Filed: November 11, 2009, Published: March 4, 2010.
- **b.** U.S. Patent 7,670,984, "*Hydrocarbon-Soluble Molybdenum Catalyst Precursors and Methods for Making Same*", Inventors: Wu, Z., Zhou, Z. and Zhou, B., Assignee: Headwaters Technology Innovation, LLC, Filed: January 6, 2006, Granted: March 2, 2010.
- **c.** U.S. Patent Application 20090308792, "Catalyst and Method for Hydrodesulfurization of Hydrocarbons", Inventor: Wu, Z., Zhou, Z. and Zhou, B., Assignee: Headwaters Technology Innovation, LLC, Filed: June 17, 2008, Published December 17, 2009.
- **d.** U.S. Patent Application 20090310435, "Mixing Systems for Introducing a Catalyst Precursor into a Heavy Oil Feedstock", Inventor: Lott, R. and Chang, Y., Assignee: Headwaters Heavy Oil, LLC, Filed: August 15, 2009, Published December 15, 2009.
- e. U.S. Patent Application 20090107881, "Methods for Increasing Catalyst Concentration in Heavy Oil and Coal/Resid Hydrocracker", Inventor: Lott, R. and Chang, Y., Assignee: Headwaters Heavy Oil, LLC, Filed: April 30, 2009.
- **f.** U.S. Patent 7,578,928, "*Hydroprocessing Method and System for Upgrading Heavy Oil Using a Colloidal or Molecular Catalyst*", Inventors: Lott, R. and Lee, L.K., Assignee: Headwaters Heavy Oil, LLC, Filed: April 28, 2005, Granted: August 25, 2009.

- g. U.S. Patent 7,517,446, "Fixed Bed Hydroprocessing Methods and Systems and System Methods for Upgrading an Existing Fixed Bed System", Inventors: Lott, R., Lee, L.K. and Quinn, P., Assignee: Headwaters Heavy Oil, LLC, Filed: April 28, 2005, Granted: April 14, 2009.
- **h.** U.S. Patent 7,449,103, "*Ebullated Bed Hydroprocessing Methods and Systems and Methods of Upgrading an Existing Ebullated Bed System*", Inventors: Lott, R. and Lee, L.K., Assignee: Headwaters Heavy Oil, LLC, Filed: April 28, 2005, Granted: November 11, 2008.
- i. U.S. Patent Application 20080193345, "*Ebullated-Bed Hydroprocessing Systems*", Inventors: Zhou, B., Zhou, Z. and Wu, Z., Assignee: Headwaters Heavy Oil, LLC, Filed: August 14, 2008.
- j. U.S. Patent Application 20070158236, "Hydrocarbon Soluble Bimetallic Catalyst Precursors and Methods for Making Same", Inventors: Zhou, B., Zhou, Z. and Wu, Z., Assignee: Headwaters Heavy Oil, LLC, Filed: July 12, 2007.
- **k.** U.S. Patent 5,578,197 "Hydrocracking Process Involving Colloidal Catalyst Formed in Situ", Inventors: Cyr, T., Lewkowicz, I., Ozum, B., Lott, R. And Lee, L.K., Assignee: Alberta Oil Sands Technology & Research Authority, Filed: April 11, 1994, Granted: November 26, 1996.

5. Heavy Residue Hydroconversion (HRH) by Mobis Energy

a. U.S. Patent 7,585,406, "*Process for Hydroconverting of a Heavy Hydrocarbonaceous Feedstock*", Inventors: Khadzhiev, S., et al, Assigned to Research Institute of Petroleum Industry (Iran) and NTI Company (Russia), Filed: August 16, 2006, Granted: September 8, 2009.

6. OrCrude Process by OPTI Canada

- **a.** U.S. Patent 7,407,571, "*Method of and Apparatus for Upgrading and Gasifying Heavy Hydrocarbon Feeds*", Inventor: Rettger, P., et al, Assigned to Ormat Industries Ltd., Filed: October 25, 2004, Granted: August 5, 2008.
- **b.** U.S. Patent 7,297,250, "*Method of and Apparatus for Processing Heavy Hydrocarbon Feeds*", Inventor: Bronicki, L., Assigned to Ormat Industries Ltd., Filed: October 25, 2004, Granted: November 20, 2007.
- **c.** U.S. Patent 7,101,499, "*Method of and Apparatus for Producing Pellets from Heavy Hydrocarbon Liquids*", Inventors: Bronicki, L, Friday, J. and Rettger, P., Assigned to Ormat Industries Ltd., Filed: July 27, 2000, Granted: September 5, 2006.

- **d.** U.S. Patent 6,702,936, "*Method of and Apparatus for Upgrading and Gasifying Heavy Hydrocarbon Feeds*", Inventors: Rettger, P., Goldstein, R. and Arnold, J., Assigned to Ormat Industries Ltd., Filed: December 26, 2001, Granted: March 9, 2004.
- e. U.S. Patent 6,274,032, "Method of and Means for Upgrading Hydrocarbons Containing Metals and Asphaltenes", Inventors: Hood, R., Rettger, P., Goldstein, R. and Bronicki, L., Assigned to Ormat Industries Ltd., Filed: July 9, 1999, Granted: August 14, 2001.
- **f.** U.S. Patent 6,274,003, "Apparatus for Upgrading Hydrocarbon Feeds Containing Sulfur, Metals and Asphaltenes", Inventors: Friday, J., Retteger, P. and Goldstein, R, Assigned to Ormat Industries Ltd., Filed: September 3, 1998, Granted: August 14, 2001.
- g. U.S. Patent 6,183,627, "Process and Apparatus for Upgrading Hydrocarbons Containing Metals and Asphaltenes", Inventors: Friday, J., Rettger, P. and Goldstein, R, Assigned to Ormat Industries Ltd., Filed: March 3, 1999, Granted: February 6, 2001.
- **h.** U.S. Patent 5,976,361, "*Method of and Means for Upgrading Hydrocarbons Containing Metals and Asphaltenes*", Inventors: Hood, R., et al, Assigned to Ormat Industries Ltd., Filed: August 13, 1997, Granted: November 2, 1999.
- i. U.S. Patent 5,944,984, "Solvent Deasphalting Unit and Method for Using the Same", Inventors: Benguigui, I., Hood, R. and Rettger, P., Assigned to Ormat Industries Ltd., Filed: March 20, 1996, Granted: August 31, 1999.
- **j.** U.S. Patent 5,919,355, "*Method and Apparatus for Processing Heavy Hydrocarbons*", Inventor: Hood, R., Assigned to Ormat Industries Ltd., Filed: May 23, 1997, Granted: July 6, 1999.
- **k.** U.S. Patent 5,914,010, "Apparatus for Solvent Deasphalting Residual Oil Containing Asphaltenes", Inventors: Hood, R. and Rettger, Assigned to Ormat Industries Ltd., Filed: September 19, 1996, Granted: June 22, 1999.
- **I.** U.S. Patent 5,843,302, "Solvent Deasphalting Unit Capable of Generating Power", Inventor: Hood, R., Assigned to Ormat Process Technologies, Inc., Filed: December 12, 1996, Granted: December 1, 1996.
- m. U.S. Patent 5,814,286, "Apparatus for Separating Solvent in a Feed of Solvent and Deasphalted Oil", Inventors: Hood, R., Rettger, P. and Bronicki, L., Assigned to Ormat Process Technologies, Inc., Filed: August 22, 1996, Granted: September 29, 1998.
- n. U.S. Patent 5,804,060, "Method of and Apparatus for Producing Power in Solvent Deasphalting Units", Inventors: Hood, R., Rettger, P. and Benguigui, I., Assigned to Ormat Process Technologies, Inc., Filed: December 13, 1995, Granted: September 8, 1998.

7. Uniflex Process by UOP

- **a.** U.S. Patent Application 20090326304, "*Process for Using Catalyst with Nanometer Crystallites in Slurry Hydrocracking*", Inventors: Bhattacharyya, G. and Mezza, B., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- **b.** U.S. Patent Application 20090326303, "*Process for Using Iron Oxide and Alumina Catalyst for Slurry Hydrocracking*", Inventors: Bhattacharyya, G. and Mezza, B., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- **c.** U.S. Patent Application 20090326302, "*Process for Using Alumina Catalyst in Slurry Hydrocracking*", Inventors: Bhattacharyya, G. and Mezza, B., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- **d.** U.S. Patent Application 20090325789, "Catalyst Composition with Nanometer Crystallites for Slurry Hydrocracking", Inventors: Bhattacharyya, G. and Mezza, B., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- e. U.S. Patent Application 20090321316, "*Process for Using Catalyst with Rapid Formation of Iron Sulfide in Slurry Hydrocracking*", Inventors: Bhattacharyya, G. and Mezza, B., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- **f.** U.S. Patent Application 20090321315, "*Process for Using Hydrated Iron Oxide and Alumina Catalyst for Slurry Hydrocracking*", Inventors: Bhattacharyya, G., Bricker, M., Mezza, B. and Bauer, L., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- g. U.S. Patent Application 20090321314, "Process for Using Iron Oxide and Alumina Catalyst with Large Particle Diameter for Slurry Hydrocracking", Inventors: Bhattacharyya, G., Bricker, M., Mezza, B. and Bauer, L., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- h. U.S. Patent Application 20090321313, "Process for Determining Presence of Mesophase in Slurry Hydrocracking", Inventors: Bhattacharyya, G., Ringwelski, A. and Mezza, B., Assignee: Honeywell/UOP, Filed: June 30, 2008, Published: December 31, 2009.
- i. U.S. Patent Application 20090127161, "*Process and Apparatus for Integrated Heavy Oil Upgrading*", Inventors: Haizmann, R. and McGehee, J., Assignee: Honeywell/UOP, Filed: November 19, 2007, Published: May 21, 2009.
- **j.** U.S. Patent Application 20090129998, "*Apparatus for Integrated Heavy Oil Upgrading*", Inventors: Haizmann, R. and McGehee, J., Assignee: Honeywell/UOP, Filed: November 19, 2007, Published: May 21, 2009.

- **k.** U.S. Patent 6,517,706, "*Hydrocracking of Heavy Hydrocarbon Oils with Improved Gas and Liquid Distribution*", Inventors: Pruden, B. and Benham, K., Assignee: Petro-Canada, Filed: May 1, 2000, Granted: February 11, 2003.
- **1.** U.S. Patent 6,004,453, "Hydrocracking of Heavy Hydrocarbon Oils with Conversion Facilitated by Recycle of Both Heavy Gas Oil and Pitch", Inventors: Pruden, B., Roy, M. and Benham, K., Assignee: Petro-Canada, Filed: March 6, 1998, Granted: December 21, 1999.
- m. U.S. Patent 5,972,202, "Hydrotreating of Heavy Hydrocarbon Oils with Control of Particle Size of Particulate Additives", Inventors: Pruden, B. and Benham, K., Assignee: Petro-Canada, Filed: March 13, 1997, Granted: October 26, 1999.
- **n.** U.S. Patent 5,755,955, "*Hydrocracking of Heavy Hydrocarbon Oils with Conversion Facilitated by Control of Polar Aromatics*", Inventors: Pruden, B., Roy, M. and Benham, K., Assignee: Petro-Canada, Filed: December 21, 1995, Granted: May 26, 1998.
- o. U.S. Patent 5,374,348, "Hydrocracking of Heavy Hydrocarbon Oils with Heavy Hydrocarbon Recycle", Inventors: Pruden, B., Sears, P., Dawson, W., de Bruijn, T. and Jain, A., Assignee: Energy Mines & Resources Canada, Filed: September 13, 1993, Granted: December 20, 1994.
- p. U.S. Patent 5,296,130, "Hydrocracking of Heavy Asphaltenic Oil in Presence of an Additive to Prevent Coke Formation", Inventors: Kriz, J., and Ternan, M., Assignee: Energy Mines & Resources Canada, Filed: January 6, 1993, Granted: March 22, 1994.
- q. U.S. Patent 5,283,217 "Production of Highly Dispersed Hydrogenation Catalysts", Inventors: Ikura, M., Stanciulescu, M. and Kelly, J., Assignee: Energy Mines & Resources Canada, Filed: June 11, 1992, Granted: February 1, 1994.
- **r.** U.S. Patent 5,120,428 "*Deashing of Heavy Hydrocarbon Residues*", Inventors: Ikura, M., Cook, N., Halevy, M. and Weber, M., Assignee: Energy Mines & Resources Canada, Filed: June 6, 1991, Granted: June 9, 1992.
- s. U.S. Patent 4,999,328 "Hydrocracking of Heavy Oils in Presence of Petroleum Coke Derived from Heavy Oil Coking Operations", Inventors: Jain, A. and Pruden, B, Assignee: Petro Canada Inc., Filed: June 28, 1988, Granted: March 12, 1991.
- **t.** U.S. Patent 4,969,988 "Antifoam to Achieve High Conversion in Hydroconversion of Heavy Oils", Inventors: Jain, A., Pruden, B., Lambiris, D., Rivard, S. and Liu, D., Assignee: Petro Canada Inc., Filed: April 17, 1989, Granted: November 13, 1990.

- **u.** U.S. Patent 4,963,247 "*Hydrocracking of Heavy Oil in Presence of Ultrafine Iron Sulphate*", Inventors: Jain, A., Belinko, K. and Khulbe, C., Assignee: Petro Canada Inc., Filed: September 7, 1989, Granted: October 16, 1990.
- v. U.S. Patent 4,923,838 "Process for Preparing an Iron-Coal Slurry Catalyst for Hydrocracking Heavy Oils", Inventors: Khulbe, C., Belinko, K., Waugh, R. and Perreault, M., Assignee: Petro Canada Inc., Filed: February 1, 1989, Granted: May 8, 1990.
- w. U.S. Patent 4,435,280 "Hydrocracking of Heavy Hydrocarbon Oils with High Pitch Conversion", Inventors: Ranganathan, R., Patmore, D. and Silva, A., Assignee: Minster of Energy Canada, Filed: September 30, 1982, Granted: March 6, 1984.
- x. U.S. Patent 4,376,695 "Simultaneous Demetalization and Hydrocracking of Heavy Hydrocarbon Oils", Inventors: Belinko, K., Patmore, D., Packwood, R. and Ranganathan, R., Assignee: Minister of Energy Canada, Filed: April 23, 1981, Granted: March 15, 1983.
- y. U.S. Patent 4,370,221 "Catalytic Hydrocracking of Heavy Oils", Inventors: Patmore, D., Ranganathan, R., Khulbe, C. and Pruden, B., Assignee: Minister of Energy Canada, Filed: March 3, 1981, Granted: January 25, 1983.
- **z.** U.S. Patent 4,214,977 "*Hydrocracking of Heavy Oils Using Iron Coal Catalysts*", Inventors: Ranganathan, R., Denis, J. and Pruden, B., Assignee: Minister of Energy Canada, Filed: March 14, 1979, Granted: July 29, 1980.
- **aa.** U.S. Patent 4,176,051 "*Process for Catalytically Hydrocracking a Hydrocarbon Oil*", Inventors: Terman, M. and Parsons, B., Assignee: Minister of Energy Canada, Filed: November 9, 1978, Granted: November 27, 1979.

8. Vacuum Resid Slurry Hydrocracking (VRSH) by Chevron

- **a.** U.S. Patent 7,678,732, "*Highly Active Slurry Catalyst Composition*", Inventors: Chen, K., Pak, C., Reynolds, B. and Farshid, D., Assignee: Chevron U.S.A. Inc., Filed: September 17, 2008, Granted: March 16, 2010.
- **b.** U.S. Patent Application 20090163352, "Conversion of Fine Catalyst into Coke-Like Material", Inventors: Powers, C., Mohr, D., Reynolds, B. and Lopez, J., Assignee: Chevron U.S.A. Inc., Filed: December 20, 2007, Published: December 25, 2009.

- **c.** U.S. Patent Application 20090163348, "*Recovery of Slurry Unsupported Catalyst*", Inventors: Da Costa, A. and Bryan, P., Assignee: Chevron U.S.A. Inc., Filed: December 20, 2007, Published: June 25, 2009.
- **d.** U.S. Patent Application 20090163347, "*Recovery of Slurry Unsupported Catalyst*", Inventors: Shah, L., Powers, C., Stoy, J., Brent, F. Reynolds, F. and Da Costa, A., Assignee: Chevron U.S.A. Inc., Filed: December 20, 2007, Published: June 25, 2009.
- e. U.S. Patent Application 20090162266, "Device for a Reactor and Method for Distributing a Multi-Phase Mixture in a Reactor", Inventor: Kemoun, A., Assignee: Chevron U.S.A. Inc., Filed: December 19, 2007, Published: June 25, 2009.
- **f.** U.S. Patent Application 20090159537, "*Reactor having a Downcomer Producing Improved Gas-Liquid Separation and Method of Use*", Inventor: Kemoun, A., Assignee: Chevron U.S.A. Inc., Filed: December 19, 2007, Published: June 25, 2009.
- **g.** U.S. Patent Application 20090159506, "*Process for Extracting Bitumen using Light Oil*", Inventor: Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed: December 20, 2007, Published: June 25, 2009.
- h. U.S. Patent Application 20090159499, "Process and Apparatus for Separating Gas from Multi-Phase Mixture Being Recycled in a Reactor", Inventor: Kemoun, A., Assignee: Chevron U.S.A. Inc., Filed: December 20, 2007, Published: June 25, 2009.
- i. U.S. Patent Application 20090159495, "*Heavy Oil Conversion*", Inventor: Chen, K., Assignee: Chevron U.S.A. Inc., Filed: December 20, 2007, Published: June 25, 2009.
- **j.** U.S. Patent Application 20090159491, "Conversion of Fine Catalyst into Coke-Like Material", Inventors: Lopez, J., Powers, C. and Mohr, D., Assignee: Chevron U.S.A. Inc., Filed: December 20, 2007, Published: June 25, 2009.
- **k.** U.S. Patent 7,485,267, "*Process for Metals Recovery from Spent Catalyst*", Inventor: Marcantonio, P., Assignee: Chevron U.S.A. Inc., Filed; July 29, 2005, Granted: February 3, 2009
- **1.** U.S. Patent 7,431,831, "Integrated In-Line Pretreatment and Heavy Oil Upgrading Process", Inventors: Farshid, D. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed; December 16, 2005, Granted: October 7, 2008.
- m. U.S. Patent 7,431,824, "Process for Recycling an Active Slurry Catalyst Composition in Heavy Oil Upgrading", Inventors: Chen, K. and Chabot, N., Assignee: Chevron U.S.A. Inc., Filed; September 10, 2004, Granted: October 7, 2008.

- **n.** U.S. Patent 7,431,823, "*Process for Upgrading Heavy Oil Using a Highly Active Slurry Catalyst Composition*", Inventors: Farshid, D. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed; December 16, 2005, Granted: October 7, 2008.
- o. U.S. Patent 7,431,822, "Process for Upgrading Heavy Oil using a Reactor with a Novel Reactor Separation System", Inventors: Farshid, D., Murphy, J. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed; December 16, 2005, Granted: October 7, 2008.
- **p.** U.S. Patent 7,410,928, "*Highly Active Slurry Catalyst Composition*", Inventors: Farshid, D., Leung, P. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed; January 16, 2007, Granted: August 12, 2008.
- **q.** U.S. Patent 7,396,799, "*Highly Active Slurry Catalyst Composition*", Inventors: Chen, K. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed; January 26, 2007, Granted: July 8, 2008.
- **r.** U.S. Patent 7,390,398, "*Process for Upgrading Heavy Oil Using a Highly Active Slurry Catalyst Composition*", Inventors: Farshid, D. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed; December 16, 2005, Granted: June 24, 2008.
- s. U.S. Patent 7,238,273, "Process for Upgrading Heavy Oil Using a Highly Active Slurry Catalyst Composition", Inventors: Chen, K., Leung, P. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed; September 16, 2004, Granted: July 3, 2007.
- t. U.S. Patent 7,214,309, "*Process for Upgrading Heavy Oil Using a Highly Active Slurry Catalyst Composition*", Inventors: Chen, K., Leung, P., Reynolds, B. and Chabot, J., Assignee: Chevron U.S.A. Inc., Filed; September 16, 2004, Granted: May 8, 2007.
- u. U.S. Patent Application 20080156700, "Process for Recovering Ultrafine Solids from a Hydrocarbon Liquid", Inventors: Abulnaga, B., Guitian, J. and Lindsay, S., Assignee: Chevron U.S.A. Inc., Filed: December 29, 2006, Published: July 3, 2008.
- v. U.S. Patent Application 20080135450, "Integrated Unsupported Slurry Catalyst Preconditioning Process", Inventors: Reynolds, B. and Brait, A., Assignee: Chevron U.S.A. Inc., Filed: December 6, 2006, Published: June 12, 2008.
- w. U.S. Patent Application 20070227947, "*T-6604 Full Conversion Hydroprocessing*", Inventor: Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed: March 30, 2006, Published: October 4, 2007.
- **x.** U.S. Patent Application 20070209967, "*Process for Producing Tailored Synthetic Crude Oil that Optimize Crude Slates in Target Refineries*", Inventor: Allinson, P. and Munson, C., Assignee: Chevron U.S.A. Inc., Filed: March 10, 2006, Published: September 13, 2007.

- y. U.S. Patent Application 20070140927, "Reactor for Use in Upgrading Heavy Oil Admixed with a Highly Active Catalyst Composition in a Slurry", Inventor: Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed: December 16, 2005, Published: June 21, 2007.
- **z.** U.S. Patent Application 20070138059, "*Integrated Heavy Oil Upgrading Process and In-Line Hydrofinishing Process*", Inventor: Farshid, D. and Reynolds, B., Assignee: Chevron U.S.A. Inc., Filed: April 24, 2006, Published: June 21, 2007.