Conversion of Australian Coals

Using a unique process developed within the Southern Illinois University to convert Victorian Brown Coal into useful products.

Thermaquatica The process developer

Greenpower Energy Ltd. Building the planet

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PROCESS

Continuous OHD Reactor System

Oxidative Hydrothermal Dissolution (OHD) works by reacting macromolecular organic solids such as coal or lignocellulosic biomass (among others) with small amounts of oxygen (O2) in liquid water at elevated temperatures and pressures. This results in oxidative cleavage of reactive structures within the macromolecular structure, producing a suite of low molecular weight, water soluble organic products. Conversion is readily taken to completion in reasonable reaction times with approximately 70 to +90% recovery of the initial carbon as water soluble products that can be refined into a variety of useful low molecular weight products. OHD has been extensively tested at the laboratory scale for a variety of coals spanning the entire rank range and also on a range of different types of biomass.

Coal, an enormously abundant resource, can be generally described as a macromolecular organic solid. Its structural characteristics vary with rank and maceral composition, but it can be generally described as consisting of aromatic clusters (consisting of variable numbers of aromatic rings) linked together with aliphatic and ether bridges, within which is occluded variable amounts of low molecular weight (MW) materials. In most cases coal also includes variable amounts of inorganic materials present as either discrete mineral phases or as exchanged cations. Because of its nature it cannot easily be refined and is primarily used as a solid fuel for energy production. The value of coal as a resource could be considerably increased if methods to disrupt its macromolecular structure could be developed.

Various strategies, including pyrolysis, gasification and direct liquefaction, have been attempted with the goal of breaking up the macromolecular structure of coal to produce low MW products that can be refined into various types of higher value products, including liquid fuels and chemicals. OHD is a novel and highly effective approach to achieving this goal. A fully continuous OHD reactor, illustrated in Figure 1, has been constructed and successfully demonstrated.

Sponsored research is now being performed on specific types of both coal and biomass for commercial development using identical equipment and general methods to those described here. Greenpower Energy of Australia is funding a Thermaquatica development programme aimed at producing a design for a pilot plant to be built in Australia using Victorian Brown Coal (VBC). Commissioning of this plant is planned for 2015. It will produce chemicals for biodegradable plastic manufacture, feedstock for fuels and specialty chemicals such as vanilla.

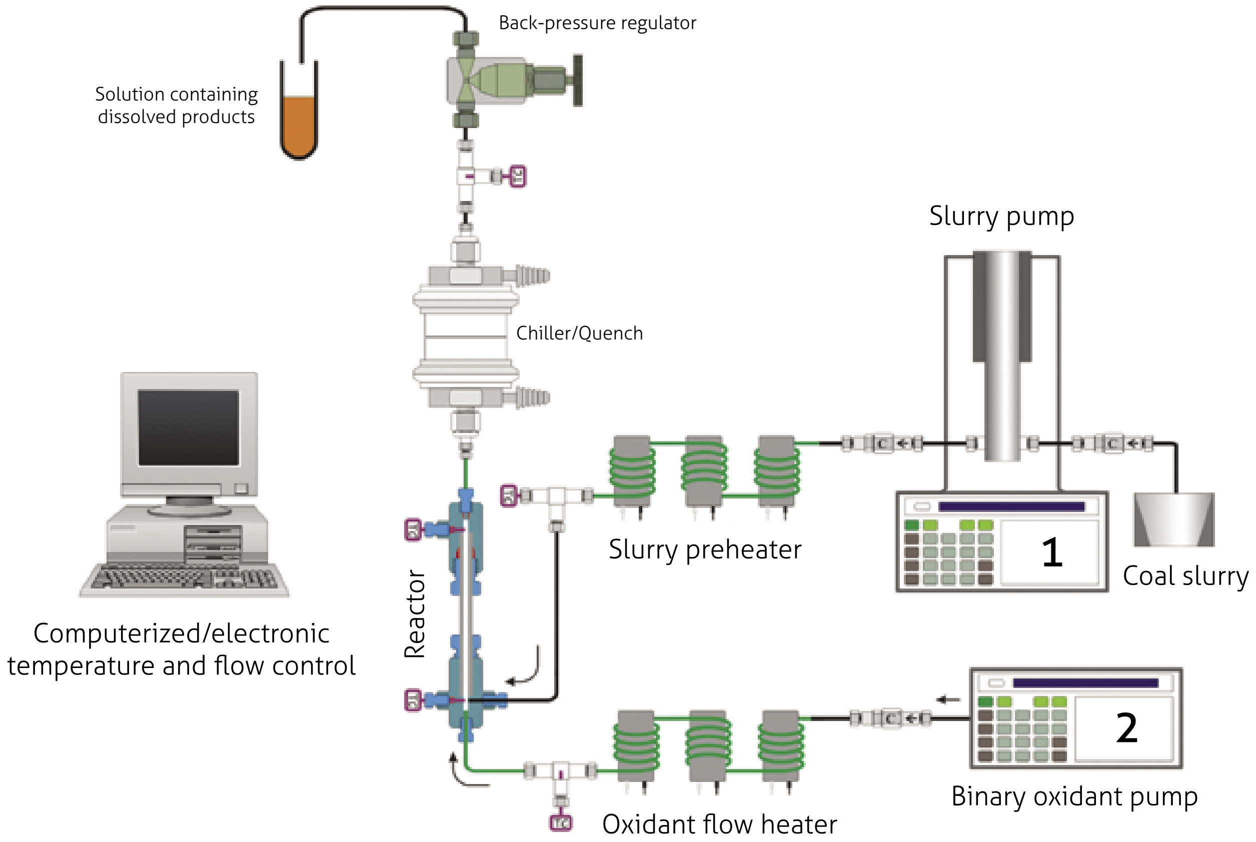

Figure 1.
Schematic of continuous OHD micro reactor system built and operated at Southern Illinois University Carbondale.

TECHNOLOGY

Thermaquatica has developed and patented a simple and inherently environmentally friendly technology called Oxidative Hydrothermal Dissolution (OHD) for the conversion of low value complex macromolecular feedstocks into high value low molecular weight products.

What is OHD?

OHD works by taking advantage of the unique properties of water at elevated temperatures and pressures and the propensity of many natural and synthetic organic materials to spontaneously oxidize when exposed to oxygen and water. The solid feed (for example: coal, biomass, or virtually any other solid organic material) is crushed and mixed with water to form a slurry which is them pressurized and heated. Small amounts of dissolved oxygen are introduced and allowed to react with the solid. No exotic catalysts or other solvents are required. The entire process requires only water, oxygen, and the right set of conditions.

At a molecular level, the oxygen attacks the most reactive structures first, effectively and selectively breaking apart the structure and directly producing low molecular weight products. By controlling the amount of oxygen, the contact time, and other variables, the extent of reaction can be controlled. For most feeds, essentially complete conversion of the initial feed with recovery of high yields of low molecular weight products can be readily achieved with relatively short contact times (for most materials, reaction times are of the order of a few 10's of seconds).

The nature and complexity of the products obtained depends primarily on the nature of the initial feed (biomass gives a different suite of products than coal, for example) and to some extent can be tailored by optimization of key process parameters. OHD produces very little CO_2, and no gaseous nitrogen or sulfur oxides. The initial raw product, known as "liquor", is an aqueous solution of the low molecular weight products produced by OHD. Depending on the nature of the products, and the goals of the operator, individual high value products can be isolated from the liquor, or the solublized organics can be handled as a mixture that can be further processed into fuels or other materials.

Development

Thermaquatica has successfully demonstrated OHD, for a wide variety of feeds, at the laboratory scale and is currently commissioning an engineering development scale process development unit (PDU) as a first scale up step. This PDU has already been successfully operated with excellent results for a small number of feeds and testing of additional feedstocks is planned for the near future. Thermaquatica has also signed an agreement with Australian energy producer Greenpower, to complete development work necessary for the design of a multi-ton per hour demonstration facility, variously described as Pilot Plant (PP) or Commercial Demonstration Unit (CDU), to be located near Greenpower's resources in Australia.

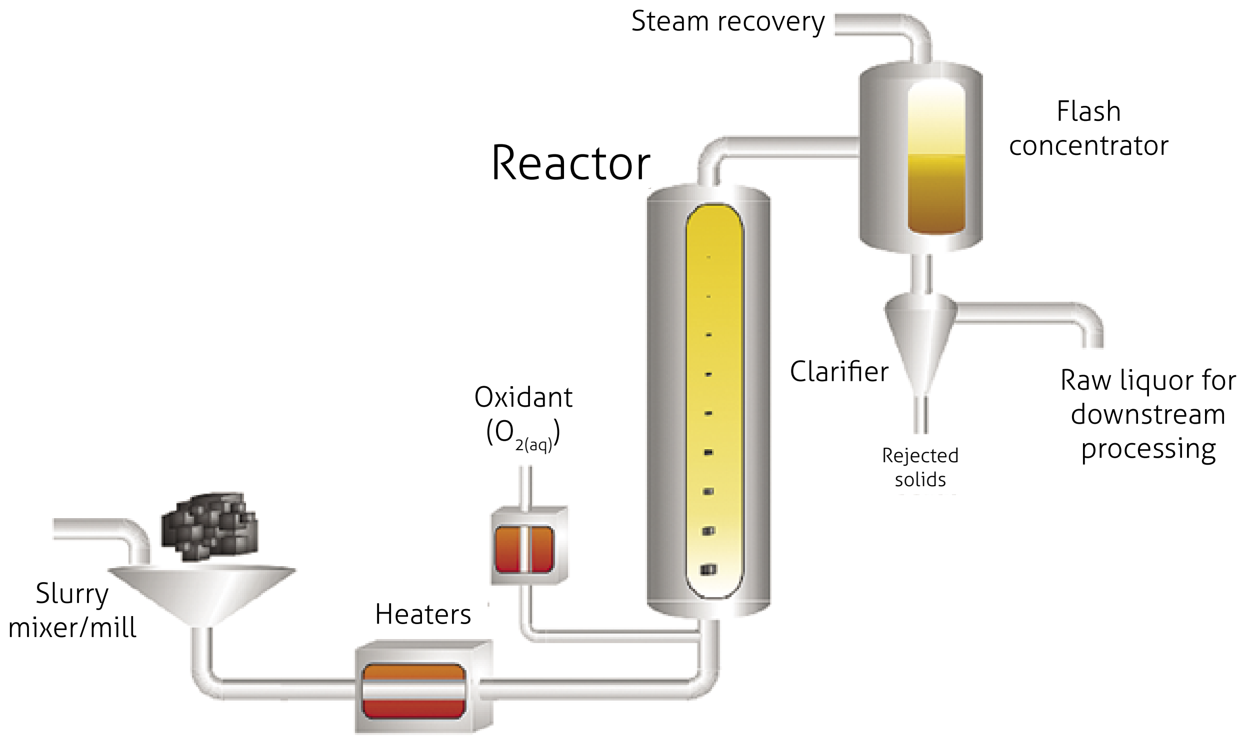

Figure 2.
Pictorial diagram for the OHD unit (see Fig 3).

PROCESS DEVELOPMENT UNIT – PDU

Continuous OHD Reactor System

The OHD technology has been demonstrated at the bench scale on both batch and fully continuous reactors. The process uses subcritical liquid water, not only as the reaction medium and solvent, but also to transport the feed and oxidant to the reactor. The PDU design is such that the central processing unit for the upscale pilot plant will have much in common with it.

The process uses an oxidative, rather than a reductive step. This means carbon is not rejected, as with other similar processes, and a hydrogen/methane supply isn't required. By using small amounts of oxygen in water, we can readily achieve 100% conversion of the organic feed, most of which is recoverable as low molecular weight, water soluble products.

The PDU (Figure 3) uses a 10kg/hr nominal processing rate of pulverized solid feed. Contact time is usually on the order of 10's of seconds, up to ~1 minute. Up to 99% of the feed water can be recycled as steam (with heat recovery) to allow for concentration of the organic products in water. The PDU will generate larger quantities of OHD product, at the optimized conditions determined on the smaller scale reactors. Furthermore, it was designed to allow experimental optimization of parameters for various feedstocks, collection of data for techno-economic analysis and as a first step to pilot scale construction for commercial units.

Figure 3.
Process Demonstration Unit (PDU).
Nominal processing rate of 10kg/h pulverized solid feed.

MARKET

Thermaquatica has developed and patented a simple and inherently environmentally friendly technology called Oxidative Hydrothermal Dissolution (OHD) for the conversion of virtually any low value complex macromolecular feedstock into high value low molecular weight products. These products can be separated for use as bio-derived fine or bulk chemicals or further processed to yield liquid fuels. OHD can be a major factor in the global drive to reduce the use of petroleum-based chemicals and fuels.

Multiple Applications for OHD

Using only water and oxygen under the right conditions, no exotic catalysts and no other solvents, the OHD process breaks down organic biomass, hard and soft coals and other organic solids into simpler compounds that can be further processed to be used as a fuel or purified and sold as fine chemicals or chemical intermediates for the production of other products including polymers. Thermaquatica's technology can be scaled for deployment at local or at regional levels depending on the demands and production characteristics of the particular feedstock application. This flexibility makes it possible to process a variety of feedstocks as the primary raw material using OHD integrated optimally as required by local operating environments.

Coal

Coal is plentiful in many areas of the world. Depending on the local economies and regulatory environments, this resource is seen as a primary source of energy, or as an underused natural resource. OHD can effectively address this sector in an environmentally friendly way, converting coal into higher value, low molecular weight products while generating little to no CO_2. Sulfur, nitrogen, and metals remain bound as solid minerals or are captured as aqueous salts or oxides that can be eliminated by typical water treatments. Our current partners seek practical ways to extract value from coal that has come under environmental or economic pressure. A process for conversion of low-grade hydrocarbon material to higher-grade material, in particular as it applies to conversion of low rank coal to high value liquid products is of utmost importance. For example, in the Latrobe Valley of Australia, inferred deposits of lignite are estimated at over 500 billion tonnes. Greenpower Energy Ltd. is currently funding research to investigate OHD as a means to convert these large deposits of low value brown coal to liquid products that can be converted to transportation fuels, purified for sale as chemical intermediates for biodegradable plastic and specialty chemicals such as vanilla. Greenpower is also implementing a programme which aims to identify coal deposits/mines where an upgrade programme using OHD is commercially attractive and in some cases is important for the local community. For instance, a small number of tests have been carried out on Collie Coal (Western Australia). OHD holds great promise for development of new, high value products from this abundant but underutilized resource.

Biomass

All over the world, companies are looking to find ways to process waste or low value biomass in a cost-effective manner to high-value products. Sources of this biomass include waste streams from industrial processing facilities (e.g. paper production), agricultural production (corn stover, sugarcane bagasse), as well as agricultural activities or biomass harvested to be used specifically in a cellulosic

process. In all cases, the end goal is to produce a value-added revenue stream with a viable alternative that transitions away from dependence on petroleum-based chemicals and fuels. The OHD process allows the production of the bio-based products needed to create chemicals and fuels demanded by the markets. The pulp and paper, agribusiness, food and beverage, as well as, waste management industries can all benefit from this process by leveraging innovation to create additional co-products and opportunities that can be used internally or moved further down the value chain.

TEAMS

THERMAQUATICA

John McAlister, PhD – CEO

Dr. McAlister is an experienced senior executive who has worked extensively in the high technology and life science industries. With a doctorate in Biochemistry, extensive experience developing and commercializing productivity solutions that combine scientific research and technology, and more than a decade as the Chief Executive Officer and Board Member of public companies, Dr. McAlister brings a unique combination of knowledge and skills to organizations on the cutting edge of innovation.

Ken Anderson, PhD – CTO

Dr. Anderson is founder of Thermaquatica. He developed the OHD concept, and has served as PI on four grants funded by the Illinois Clean Coal Institute to explore the concept and develop the fundamental technology. He is an organic geochemist with more than 20 years of experience in coal science and related areas. He currently holds the rank of full professor in the Department of Geology, at SIUC. Dr. Anderson received his PhD in coal chemistry from the University of Melbourne, Australia, in 1989. Prior to joining SIUC, he was a research scientist at Argonne National Laboratory, in the coal chemistry research group from 1994-2003. Prior to that, he worked for Amoco Oil Company from 1991-1994, conducting proprietary research on coal liquefaction and heavy oil processing. He holds five patents, many of which are in commercial application.

Bia Thomas, PhD – Business Operations

Dr. Thomas is an entrepreneur who brings energy related academic research as well as industry experience to Thermaquatica. Her doctorate in energy, environmental and chemical engineering has given her the tools to efficiently evaluate business opportunities and assist in the derisking process of disruptive technologies. Most recently, Dr. Thomas was the Senior Control Systems Engineer at a successful solar energy startup that was acquired in 2011. She has provided chemical engineering, project management oversight and consulting at multiple processing plants in the instrumentation, automation and energy sectors. A native of Brazil, she is fluent in Portuguese and Spanish as well as English. She assumes the role of Business Operations at Thermaquatica and will be responsible for operational and logistical aspects of the business.

Derek Perry – Process Engineer

Mr. Perry is lead equipment and process engineer for the OHD development team at Thermaquatica. He began preliminary lab-scale OHD studies in 2009, working as a post-graduate researcher, and, in 2011, became the first full-time employee of Thermaquatica. While managing the bench-scale research, Mr. Perry became the principal investigator on a Illinois Clean Coal Institute (ICCI) funded grant for design and construction of a pilot-scale OHD unit. Mr. Perry holds a masters degree in Mechanical Engineering and Energy Processes from SIUC. His graduate research involved development of clean coal technologies associated with gasification and Fischer-Tropsch synthesis.

Madhav Soti – Engineer

Mr. Soti was appointed as an Engineer for Thermaquatica in August 2013. As an Engineer, he is responsible for operating, modifying and performing experimental work in the Process Development Unit (PDU) for further development of the OHD process. He completed his Bachelor's degree and is pursuing his MSc in Mechanical Engineering and Energy Process from Southern Illinois University, Carbondale. His specific research interests are in the area of Fischer-Tropsch processes specifically enhancing the production of liquid fuels and direct liquefaction of coal with supercritical CO_2.

GREENPOWER

Gerard King – Director, Administrative Executive

Gerard King guides the corporate trajectory of the company. He graduated from law from the University of Western Australia, then after articles with Sir John Lavan was admitted as a solicitor in 1965. Gerard practised law in the areas of commercial contracting/property, banking/finance, revenue/tax, corporate and ASX compliance and mining law. He has been a director of a number of listed companies including Australian Mining Investments 1983 to 2002 and is currently Chairman of Directors of Astron Ltd [ASX:ATR].

Alan Flavelle – Executive Chairman, Principal Geological and Technical Consultant

Alan Flavelle develops the technical direction of the company. He is a science graduate from the University of Western Australia with a major in physics. Since graduation he has been continuously involved, with government and private industry, in mineral and energy resource development. He first worked in Gippsland on the geological structure of the basin in 1959 and has maintained an interest in the commercial development of the Victorian Brown Coal. Since 2008 he has examined a number of coal conversion technologies and was part of a team that recommended to Greenpower that they become involved in its commercial development.

Martin L. Gorbaty , PhD – Principal, Fuels Science Consulting, LLC

Martin L. Gorbaty earned his Ph. D. in organic chemistry from Purdue University in 1969, after which he joined ExxonMobil and worked in research and management until his retirement as a Distinguished Research Associate in 2006. His career focused on the chemistry and processing of heavy oils, coals and oil shale into clean hydrocarbon fuels and chemicals. He is an inventor on 61 United States Patents, has published 80 technical papers, given 77 invited lectures and edited 5 books on coal and synthetic crudes. He has received many awards and recognitions for his research work, including the Henry H. Storch Award in Fuel Chemistry from the American Chemical Society, the Distinguished Researcher Award from the Petroleum chemistry Division of the American Chemical Society and the Distinguished Alumnus Award from the School of Science of Purdue University. He was elected as a Fellow of the American Chemical Society in 2010.

Collaborative organisations in Australia

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CORPORATE INFORMATION

Thermaquatica Inc. partners with Greenpower Energy to develop Coal-to-Liquids Technology. A research agreement will fund development of Thermaquatica's novel, environmentally friendly OHD process.

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Carbonadale, IL, May 30, 2013 — Thermaquatica Inc. of Carbondale, IL, USA announces the signing of a Research and Option agreement with Greenpower Energy Limited at Thermaquatica's Headquarters on May 24th, 2013. Under terms of the agreement, Greenpower will contribute US$2 million toward further development by Thermaquatica of Oxidative Hydrothermal Dissolution (OHD), a process for conversion of low grade hydrocarbon material to higher grade material, in particular as it applies to conversion of low rank coal to high value liquid products. In return, Greenpower is granted a two-year option to take an exclusive license for the commercial application of this process within Australia and New Zealand.

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OHD is a novel, environmentally friendly technology for the conversion of coal, lignocellulosic (woody) biomass, and other organic solids into low molecular weight, water-soluble products, many of which are potentially valuable for making polymers and other hydrocarbon-based products. OHD works by reacting coal or other macromolecular organic solids with small amounts of oxygen in high-temperature, high-pressure liquid water. Professor Ken Anderson and his collaborators discovered and developed the OHD processes at the Southern Illinois University Carbondale (SIU), which owns the pending patents for this technology. Professor Anderson, Thermaquatica's Chief Technical Officer, founded Thermaquatica in late 2010 to commercially exploit this process. Thermaquatica holds the exclusive worldwide license from SIU to the patent rights. Early development of the process and an engineering scale-up Process Development Unit have been funded by a $950,000 grant from the Illinois Clean Coal Institute. Additional assistance has been provided by the SIU Technology Transfer Office and the Southern Illinois Research Park.

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Greenpower Energy Limited (www.greenpowerenergy.com.au) is a publicly traded company listed on the Australian Stock Exchange (ASX:GPP). Greenpower's mission and focus is to seek practical ways to find realistic, commercial, and effective processes to provide the increasing amounts of energy required to meet the world's needs — processes that will significantly reduce man's carbon footprint on our planet. Greenpower holds exploration mining tenements in the Latrobe Valley of Australia containing inferred deposits of lignite estimated at over 500 million tons and has been searching for appropriate processes to convert coal to liquid products in order to produce transportation fuels and other products in an environmentally friendly way.

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Commenting on this agreement, Dr. John P. McAlister, Thermaquatica's CEO stated, "The relationship with Greenpower established through this agreement empowers Thermaquatica to aggressively develop and commercially deploy OHD in a number of application areas. We are delighted to partner with Greenpower in its efforts to exploit the abundant natural resources at its disposal in a unique and environmentally friendly way."

Dr McAlister continued, "We believe this is the first in a potentially large number of applications for OHD, a process which has been demonstrated to work equally efficiently on a wide variety of biomass including wood chips, corn stover, and sugarcane bagasse, as well as oil shale, tar sands, and many others.

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Mr Gerard King, board director of Greenpower commented, "We at Greenpower are very impressed with the demonstrated capability of Thermaquatica's OHD process and with the research and engineering capabilities of the team led by Professor Ken Anderson. We look forward to bringing this technology to bear on our large resource holdings in Australia where we believe it can have a real and positive impact."

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"Thermaquatica is a great example of groundbreaking research by our outstanding faculty and their focus on helping to solve some of the world's most pressing environmental and economic challenges," SIU Chancellor Rita Cheng said. "I am pleased that our entrepreneurship programs, which encourage and guide our faculty, helped Dr. Anderson and his team achieve this level of commercial success."

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About Thermaquatica Inc.
Founded in November 2010 and located in Carbondale, Illinois, Thermaquatica is dedicated to the scale-up and commercial exploitation of the Oxidative Hydrothermal Dissolution process discovered and pioneered by Professor Ken Anderson of Southern Illinois University. Thermaquatica is merging creative chemistry with engineering to pioneer the development of environmentally friendly means to produce next generation materials and fuels.

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About Greenpower Energy Limited
With a long legacy in coal production as Gunnedah Colliery Company before changing its name and mission in 2007 to Greenpower Energy Limited, Greenpower's mission and current focus is to seek practical ways to find realistic, commercial and effective processes to create the increasing amounts of energy for today's world needs — processes that will significantly reduce man's carbon footprint on our planet. Greenpower has not limited the scope of this search in any way — for example the company is testing methods to produce and use existing fuel sources such as natural gas and coal that are practical and economic and make a real reduction in carbon emissions. Greenpower is also exploring commercially viable energy sources and production methods.

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CHEMICAL LISTS

VICTORIAN BROWN COAL
CONVERSION BY OHD PROCESS

% of total	Compound	CAS#
2.09%	Anisole	100-66-3
2.44%	Dimethyl Succinate	106-65-0
0.87%	Dimethyl, 2-Methyl succinate	1604-11-1
0.68%	Methyl Benzoate	93-58-3
0.58%	Methoxy phenol (probably 2 methoxy isomer)	150-76-5
6.43%	1,2-Dimethoxybenzene	91-16-7
0.79%	1,3-Dimethoxybenzene	151-10-0
1.99%	1,4-Dimethoxybenzene	150-78-7
1.65%	4-Methoxy Benzaldehyde	123-11-5
1.94%	Trimethoxybenzene (probably 1,2,3 isomer)	135-77-3
2.85%	Methyl 3-Methoxybenzoate	5368-81-0
0.56%	Dimethyl Pimelate	1732-08-7
1.16%	Methyl 2-Methoxybenzoate	606-45-1
12.29%	1,2,4-Trimethoxybenzene	135-77-3
0.56%	Methyl 4-Methoxybenzoate (Methylated parahydroxy benzoic acid)	121-98-2
1.01%	3-Methoxy Acetophenone	586-37-8
0.65%	Methyl 3-methoxy-4-methylbenzoate	3556-83-0
1.25%	Trimethoxybenzene (probably 1,3,5 isomer)	14107-97-2
1.34%	Dimethyl suberate	1732-09-8
1.27%	Trimethoxytoluene (probably 2,4,6 isomer)	14107-97-2
1.49%	Dimethyl azelate	1732-10-1
5.21%	3,4-dimethoxybenzaldehyde	120-14-9
0.77%	Methyl vanillate (incomplete methylation product equivalent to peak 25)	3943-74-6
4.03%	Methyl 3,5-Dimethoxybenzoate (isomer of peak 25)	25081-39-4
24.80%	Methyl veratrate (Methyl 3,4-dimethoxybenzoate)	2150-38-1
3.03%	2,4-Dimethoxyacetophenone	829-20-9
1.17%	Unassigned (possibly dimethyl phthalate)	131-11-3
0.76%	Dimethyl Sebacate	106-79-6
1.49%	Unassigned	
1.20%	3,4,5-Trimethoxybenzaldehyde	86-81-7
4.10%	Methyl 3,4,5-trimethoxybenzoate	1916-07-0
1.55%	Unassigned	
3.24%	Unassigned	
0.87%	Methyl Palmitate	112-39-0
0.80%	DIMETHYL 4-METHOXYTEREPHTHALATE	120-61-6
0.72%	Unassigned	
0.81%	Unassigned	
0.75%	Trimethyl 1,3,5-benzenetricarboxylate	2672-58-4
0.82%	Unassigned	
9.80%	Total Unassigned	
100%		

COLLIE COAL
CONVERSION BY OHD PROCESS

% of total	Compound	CAS#
1.75%	Anisole (Methoxybenzene)	100-66-3
12.83%	Methyl 3-methoxybenzoate (mHB)	5368-81-0
7.18%	Methyl 4-methoxybenzoate (pHB)	121-98-2
1.61%	Dimethyl Terephthalate	120-61-6
4.36%	Dimethyl isophthalate	1459-93-4
1.07%	6,7-Dimethoxy-m-cymene (?)	
4.79%	Methyl 3-hydroxybenzoate	19438-10-9
4.84%	Methyl 3,5-Dimethoxy benzoate	
2.42%	Methyl 3,4-Dimethoxy benzoate	24812-90-6
2.43%	Unassigned (?)	
7.63%	Dimethyl 2-Hydroxy Terephthalate	
5.82%	C3 alkyl hydroxy methoxy benzoate (unknown isomer)	
9.81%	1,7,7-trimethyl-2(1H)-Naphthalenone, octahydro-4A-(hydroxymethyl)- (*)	
1.74%	C16 FAME	
1.93%	Dimethyl 4-Methoxy Terephthalate	120-61-6
1.64%	Trimethyl trimesate (1,3,5-Benzenetricarboxylic acid, trimethyl ester)	2459a-10-1
28.15%	Trimethyl trimesate (1,3,5-Benzenetricarboxylic acid, trimethyl ester)	2672-58-4
100%		

* Peak 13 is a terpenoid derived product reflecting the probable presence of minor amounts of fossil resin within the coal.

SCIENTIFIC BASIS FOR OHD

Oxidative Hydrothermal Dissolution (OHD): An efficient, environmentally friendly process for the dissolution of coal and biomass in aqueous media, for the production of fuels and chemicals.

Ken B. Anderson[1,2,*], John C. Crelling[1,2] , William W. Huggett[2], Derek Perry[1,2], Tom Fullinghim[2], Patrick McGill[2], Paul Kaelin[2].

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Abstract

Oxidative Hydrothermal Dissolution (OHD) is a novel coal conversion technology developed with support from the Illinois Clean Coal Institute. OHD works by reaction of coal and/or biomass with small amounts of oxygen in high temperature, high pressure, liquid water. This breaks up the coal's structure, resulting in the generation of low molecular weight, water soluble products. Complete conversion of the coal is readily achievable with 70-90% recovery of the original carbon as water soluble products. Most silicate minerals present in the coal pass through the process essentially unaltered. Raw OHD product is an aqueous solution (not a colloid or suspension) consisting of a mixture of low molecular weight aromatic and aliphatic acids and related derivatives that could potentially supplement or replace some petroleum–derived products as chemical feed stocks. Raw OHD product can be pumped and refined using conventional liquid processing technology.

Since the process uses only water and oxygen, it is inherently environmentally friendly. No exotic solvents or expensive catalysts are required. It produces little CO_2, and no NO_x, SO_x or other toxic emissions. Harmful elements like mercury, arsenic etc., are not released to the environment but either remain associated with their parent minerals or are retained in the product solution and can be processed and captured by conventional waste water treatment strategies.

Introduction

Coal, an enormously abundant resource, can be generally described as a macromolecular organic solid. Its structural characteristics vary with rank and maceral composition, but it can be generally described as consisting of aromatic clusters (consisting of variable numbers of aromatic rings) linked together with aliphatic and ether bridges, within which is occluded variable amounts of low molecular weight (MW) materials. In most cases coal also includes variable amounts of inorganic materials present as either discrete mineral phases or as exchanged cations. Because of its nature it cannot easily be refined and is primarily used as a solid fuel for energy production. The value of coal as a resource could be considerably increased if methods to disrupt its macromolecular structure could be developed.

Various strategies, including pyrolysis, gasification and direct liquefaction, have been attempted with the goal of breaking up the macromolecular structure of coal to produce low MW products that can be refined into various types of higher value products, including liquid fuels and chemicals. Oxidative Hydrothermal Dissolution (OHD) is a novel and highly effective approach to achieving this goal[1]. OHD works by reaction of the coal, or other macromolecular organic solid, with small amounts of O_2, in liquid water at elevated temperatures and pressures. This results in oxidative cleavage of reactive structures in the coal, producing a suite of low MW (<~500 amu) organic products that are soluble in water. Conversion is readily taken to completion in reasonable reaction times with 70-90% recovery of the original carbon as water soluble products that can be refined into a variety of useful low MW products.

Experimental

Figure 1 illustrates a schematic of the experimental system used for micro-scale testing of OHD. This reactor system is a semi-continuous design in which a fixed charge of coal (typically 10-100mg, 20-60 mesh) can be subject to OHD under precisely controlled conditions. An additional fully continuous OHD reactor, illustrated in Figure 2, has also been constructed and successfully demonstrated.

For reasons of experimental convenience, O_2 in these reactions is typically produced in situ by thermal decomposition of H_2O_2. Testing has also been done using dissolved O_2 with identical results, but at the scale used for these experiments, reproducible generation of solutions of dissolved O_2 is experimentally cumbersome. The reaction is typically carried out at temperatures of 220-350°C with oxidant loading of 0.002-0.01 M O_2. Flow rates are varied according to experimental requirements. Reaction products can be monitored by photodiode array (PDA) detection and/or can be collected for off-line analysis by GCMS and other techniques.

Figure 1. (overleaf)
Schematic of semi-continuous micro reactor system used for testing and evaluation of OHD of coal and other organic solids.

Figure 2. (overleaf)
Schematic of continuous OHD micro reactor system built and operated at So.

Figure 1.

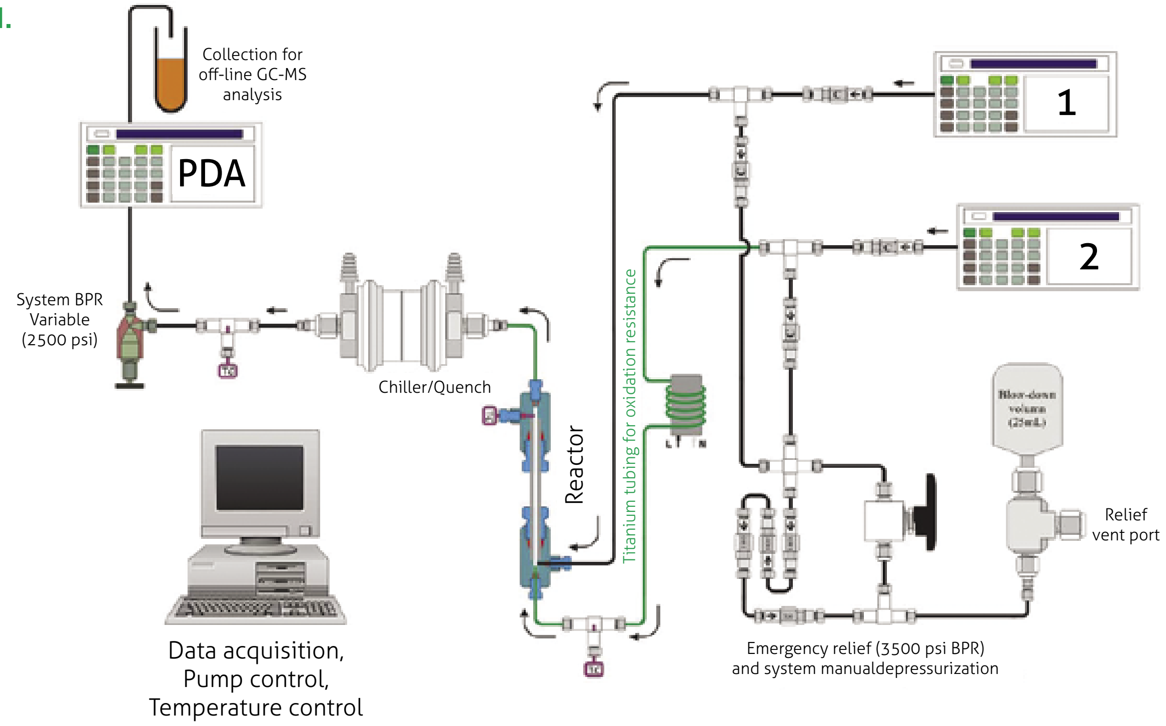
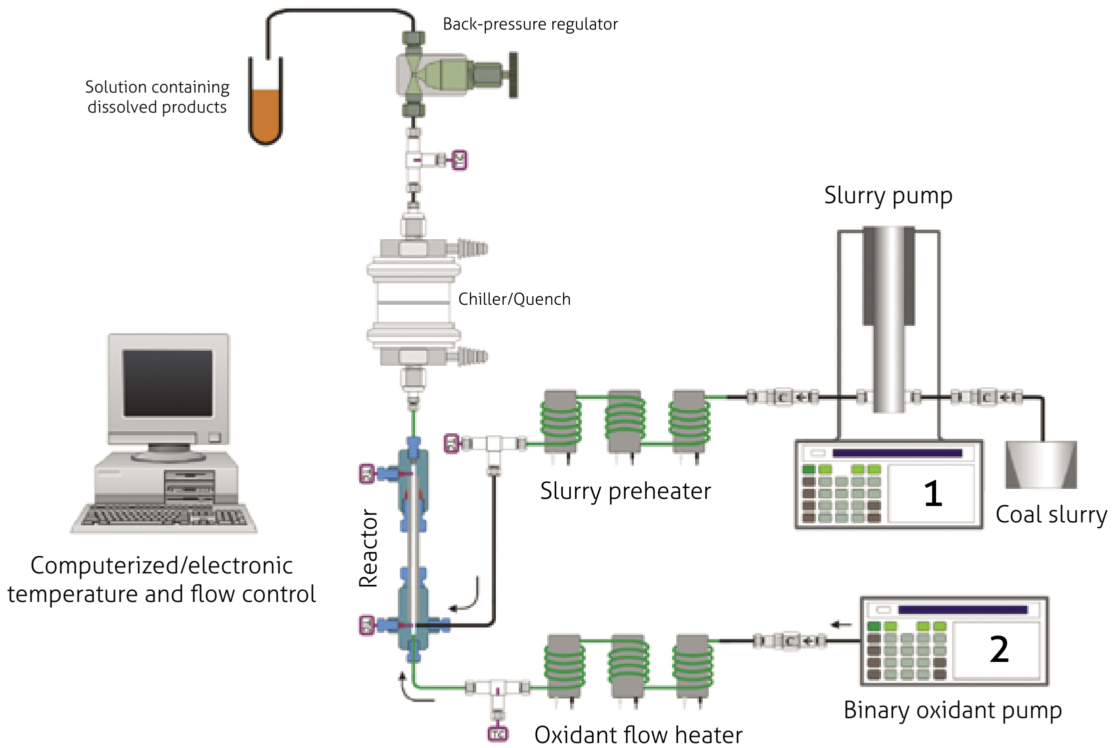


Figure 2.



Results and Discussion

The raw product (liquor) derived from OHD of bituminous coal is a clear solution of dissolved organic products. In most cases colloidal solids are absent, as illustrated in Figure 3, below, which shows both raw OHD liquor derived from dissolution of Illinois coal and a diluted product prepared by addition of water to the same raw liquor. The diluted product is a clear solution and does not contain suspended solids.

Figure 3.
Raw and diluted OHD product derived from Illinois coal.

Formation of OHD product is not the result of simple hydrolysis. Figure 4 illustrates PDA response as a function of time for an experiment in which oxidant is discontinuously delivered as six equal pulses of oxidant to a fixed charge (~10 mg) of Illinois No. 6 coal. Detector response is ~0 prior to delivery of oxidant indicating that simple hydrolysis of the coal is insignificant at these conditions over the period of the experiment. Response increases rapidly at the beginning of each pulse and decreases rapidly when oxidant is discontinued, indicating that production of dissolved product is directly related to the delivery of O_2 and that response to delivery of oxidant is rapid. No soluble or insoluble catalyst is used and no co-solvent is present.

Application of this process to a wide range of coal, biomass, and similar macromolecular organic solids (including various types of lignocellulosic biomass, lignite, bituminous coal, anthracite and wood charcoal) has been evaluated. In all cases, complete conversion of organic materials to soluble products is readily achieved, although rates of reaction vary considerably. Petrographic analyses demonstrate that dissolution of coal proceeds by etching of particle surface, as illustrated in Figure 5, which illustrates photomicrographs of anthracite before and after being subject to OHD conditions (In this case dissolution was stopped before being taken to completion).

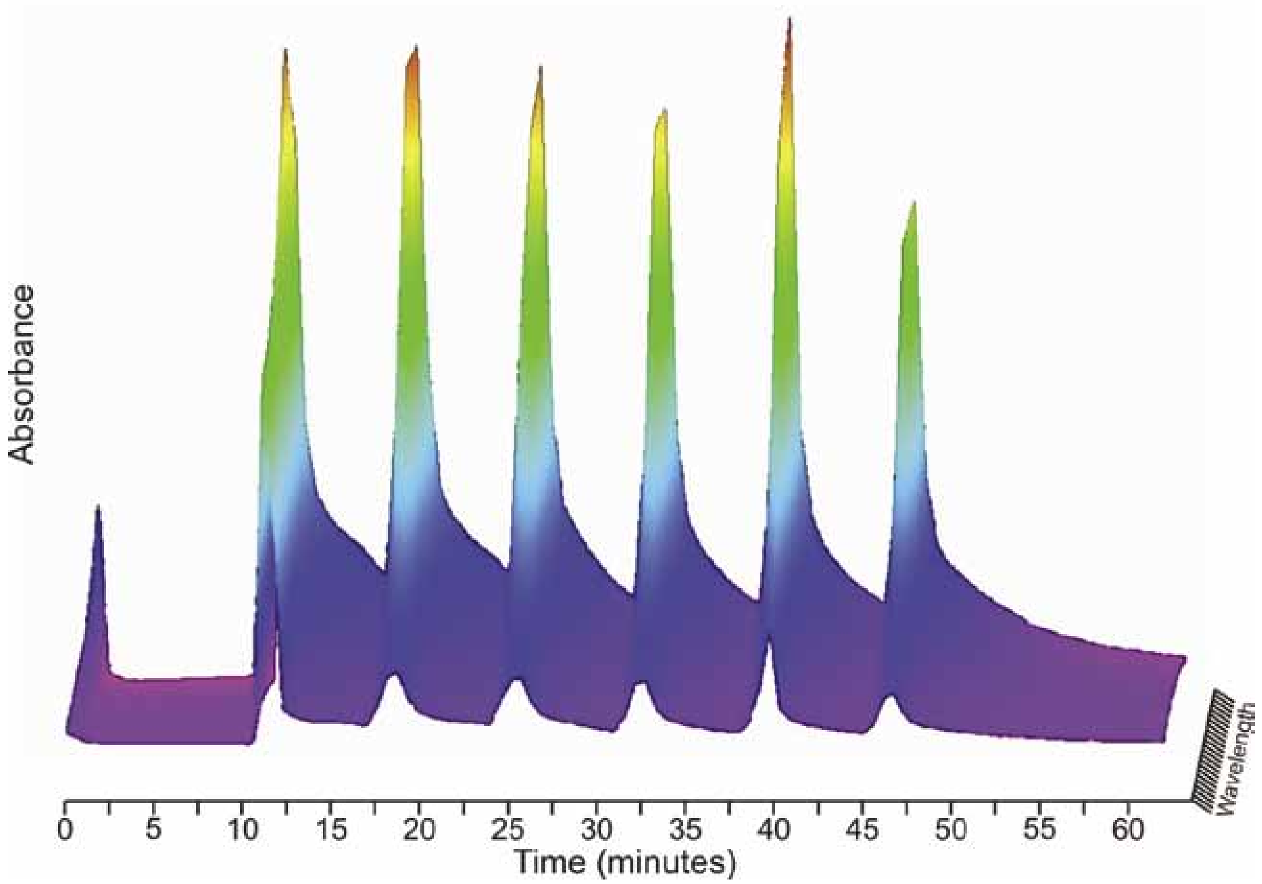


Figure 4.
PDA response for OHD of IL #6 coal, 6 pulses of oxidant delivered. Time range illustrated = 65 minutes. 10 min start delay for baseline followed by six 1 min oxidant pulses with 6 min between pulses.

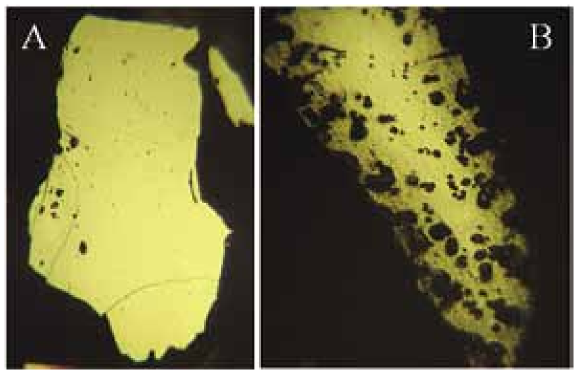


Figure 5.
Petrographic analysis comparing (A) raw anthracite and (B) residue after partial dissolution by OHD.

As expected, reaction rate is dependent on particle size, reaction temperature, oxidant loading and flow rate/contact time, as well as varying with initial substrate, but is typically of the order of minutes for complete dissolution for -20 +60-mesh bituminous coal. In general, low rank materials react faster than high rank materials, (presumably due to the more poly-condensed nature of the high rank materials), and macerals react in order liptinite>vitrinite> inertinite.

These data suggest that the process works by oxidative cleavage of labile structures, resulting in disruption of the overall macromolecular structure. As low MW products are produced they dissolve into the reaction medium (water), which at hydrothermal conditions is an excellent solvent for most organics, and are separated from residual solid, thereby exposing fresh surface for subsequent reaction with additional oxidant. Rapid removal of the water and separation of the produced organic solute or quenching prevents over-oxidation of the dissolved product.

For most raw solids, 70-90% of the initial carbon is recovered as solublized products at optimal reaction conditions. Minor amounts of gaseous products (CO and CO_2) are also generated, with CO typically dominating. No gaseous N or S oxides are generated. Inorganic N and S are retained in the aqueous phase as sulfate and nitrate, respectively. Organic S is at least partially retained as soluble organo-sulfur compounds in the product liquor.

Characterization of the solublized products indicates that these consist of moderately complex mixtures of low MW organics. For bituminous coal, these consist predominantly of:

(i) aliphatic carboxylic acids and diacids from C1 to ~C20 (in many cases acetic acid is the single most abundant product obtained and may account for up to 5-% of the raw product, depending on the initial feedstock).

(ii) mono-aromatic carboxylic acids, polyacids and phenols, including methoxylated analogues.

An example product distribution derived from Illinois coal is illustrated in Figure 6. The exact distribution of products obtained is dependent on the nature of the starting material used. For humic coals, lignites tend to give products dominated by simple aliphatic acids and diacids and monocarboxylic aromatic acids/ phenols whereas OHD products derived from higher rank coals are generally dominated by aromatic products including di- and poly-carboxylic acids and related analogues.

As expected, biomass derived OHD products tend to be simpler than those derived from coals. The distribution of compounds observed in the OHD product derived from soft wood lignin is illustrated in Figure 7. This product is dominated by three related compounds all derived from oxidative cleavage of guaiacyl lignin. Two of these are partial oxidation products and the major product, m-methoxy, p-hydroxy benzoic acid (observed in these analysis as its fully methylated analogue for analytical convienience) reflects complete oxidation of the C3 side chain of the original lignin.

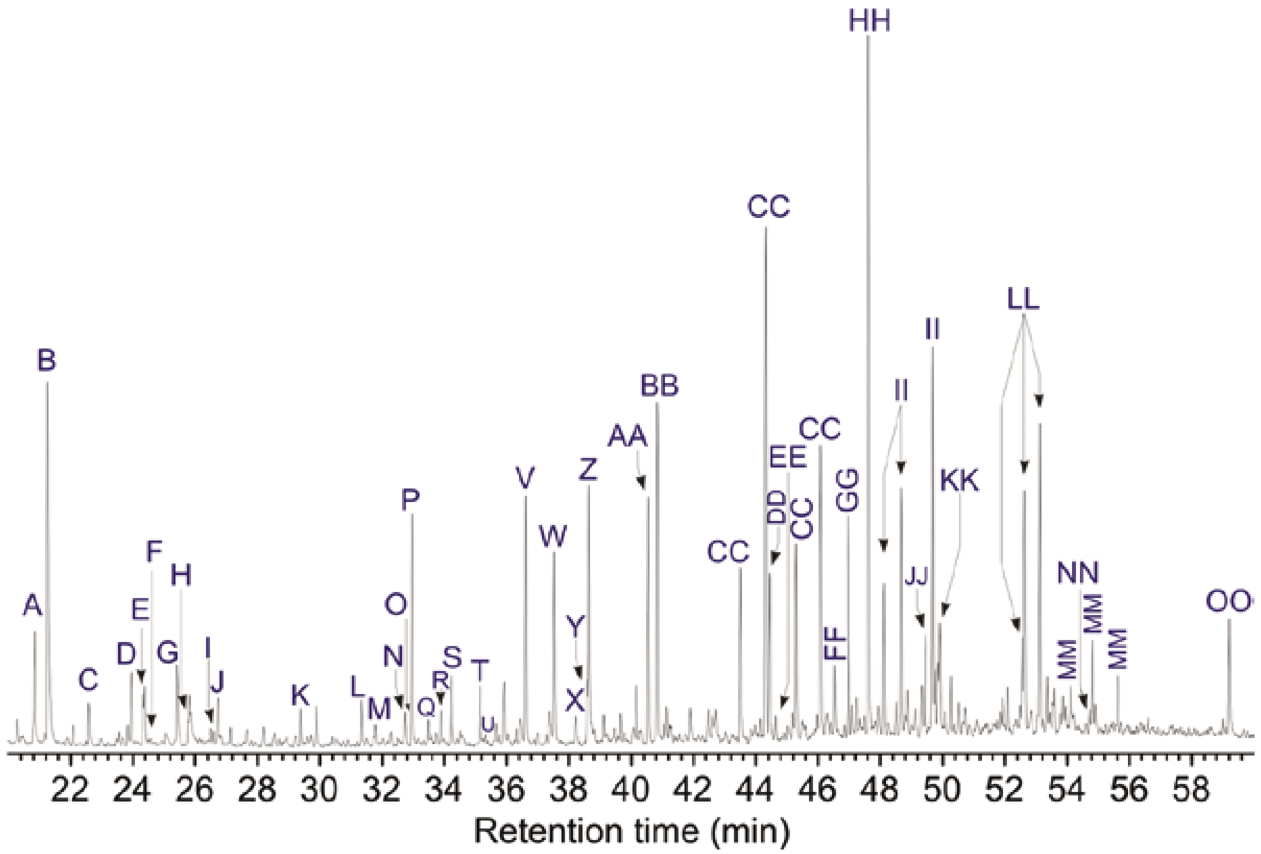


Figure 6.

Distribution of products identified in OHD product derived from Illinois #6 coal. Individual products are listed in the table below:

ID	Assignment
B	1,4-butanedioic acid
P	3-methoxy benzoic acid
V	1,2-benzene dicarboxylic acid
Z	thiophene-2,5-dicarboxylic acid
AA	3,5-dimethoxy benzoic acid
BB	3,4-dimethoxy benzoic acid
CC	methoxy benzene dicarboxylic acid (isomer undetermined)
GG	1,2,3-benzene tricarboxylic acid
HH	1,2,4-benzene tricarboxylic acid
II	dimethoxy benzene dicarboxylic acid (isomer undetermined)
LL	Unknown

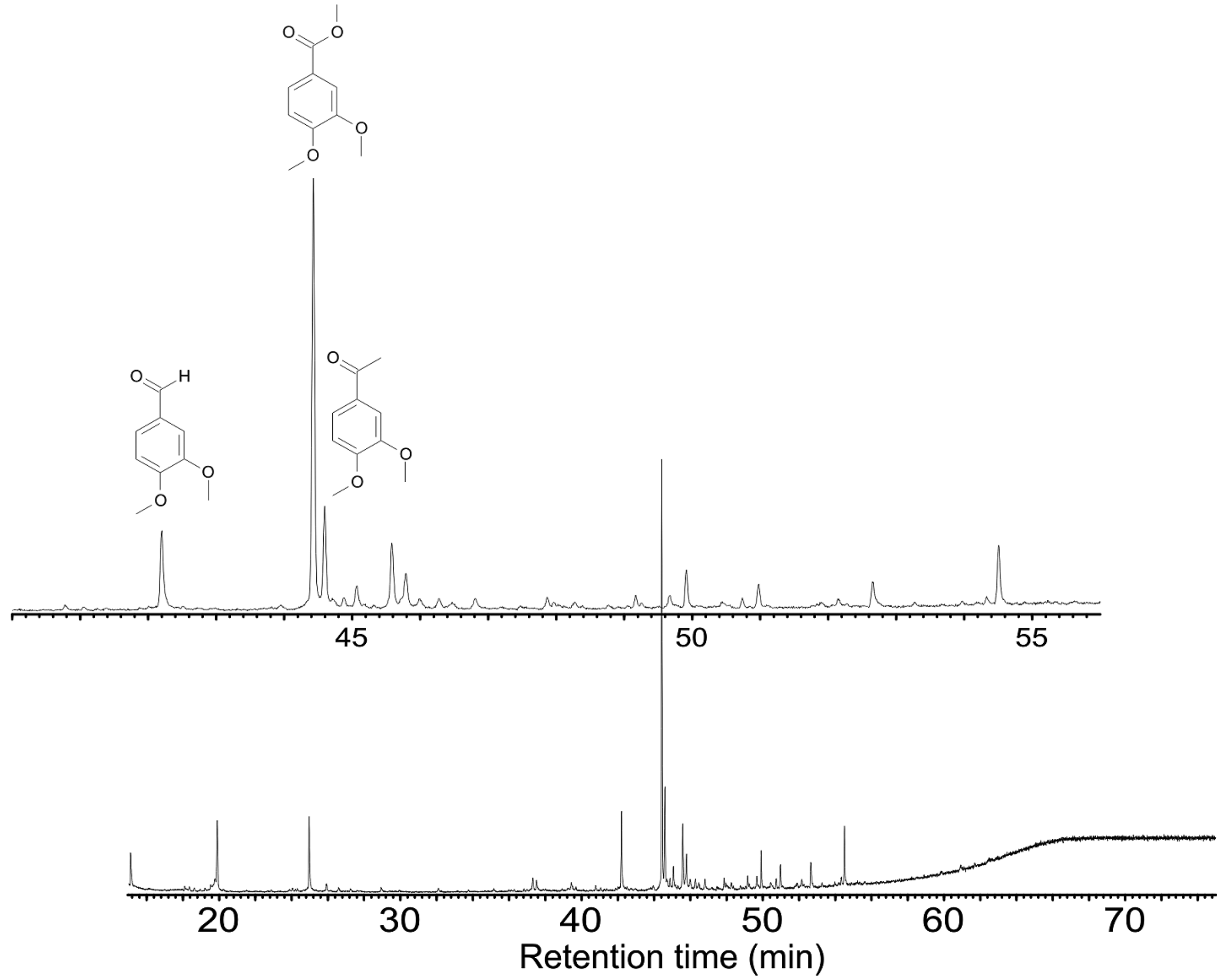


Figure 7.

OHD product of soft wood (conifer) lignin. Inset upper trace is an enlargement of time 40-57 minutes of the lower chromatogram, included for clarity. Structures of major products are indicated.

Mass spectrometric and chromatographic analyses both indicate that high (>~500 amu) MW products are absent in freshly prepared OHD products. If allowed to stand for extended periods, some precipitation does occur, presumably due to oxidative coupling (e.g. phenolic coupling) of the primary products. Raw liquor is also subject to growth of biomass if not kept completely sterile.

Silicate minerals are generally unaffected by OHD conditions and are retained unaltered in the reaction residue. Pyrite undergoes rapid oxidation (analogous to pyrite weathering related to acid mine drainage) with S released as aqueous sulfate and Fe re-precipitated as a mixed Fe(O)(OH) phase functionally equivalent to goethite. Most inorganics are retained in the solid phases with which they are initially associated in the raw coal and the remainder are retained in the aqueous phase with the solubilized organic product.

Conclusions

Oxidative Hydrothermal Dissolution is a novel conversion strategy for the efficient conversion of coal and other macromolecular solid organic materials to low MW water soluble organic products by reaction with small amounts of molecular oxygen in subcritical (liquid) water at temperatures of ~200-370°C . The process is simple and does not require use of exotic catalysts or solvents other than water. Complete dissolution of the initial coal or other macromolecular organic solid with recovery of 70-90% of the initial carbon as dissolved products is readily achievable in most cases. The process is robust and widely applicable to a broad range of substrates.

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1. Ken B. Anderson, J.C. Crelling and W.W. Huggett

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