

# ASX CODE (GPP) ABN 22 000 002 111

#### **ABOUT GREENPOWER**

Greenpower Energy is a coal to chemical technology developer progressing the development of 'zero carbon' processes for converting coal to chemicals.

Go to greenpowerenergy.com.au

#### **CAPITAL STRUCTURE**

- Shares on issue	609 m
- Unlisted options	45 m
Current:	
Cach	0.71m

- Cash U./1m - Shares in listed co .4m - Exploration assets 1.3m

#### **CONTACT US**

Alan Flavelle Chairman – 0438 599 252 Gerard King MD – 0418 852 700 Matt Suttling CFO/Secretary – 0425 215 349

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# <u>GREENPOWER DEVELOPMENT</u> PROGRESS – SHAREHOLDER UPDATE

**9 May 2016:** Greenpower Energy Limited is pleased to update shareholders on progress of the development and commercialisation of its unique coal conversion process.

This process, known as OHD (Oxidative Hydrothermal Dissolution), converts coal into low molecular weight organic compounds. Many of these products are potentially useful for producing fine chemicals, specialty chemicals, commodity chemicals, agricultural biostimulants and bio-diesel. The process uses crushed coal, water and liquid oxygen. No other materials are used and no greenhouse gases are produced.

#### **Agricultural Biostimulants**

The basic OHD reactor produces a water product that is an excellent agricultural biostimulant, used to enhance plant growth. Researchers at Monash University are conducting trials to determine the best way to apply the liquid to various commercial plant species. These trials, which are being supported by a Federal Government grant, are due for completion by the end of 2016. The company anticipates supplying these biostimulants to the agricultural sector at prices that will make them attractive to the broadacre sector.

#### Joining the Chemical Industry

Meanwhile, the company has commissioned industrial chemist expert Dr Duncan Seddon to assist Greenpower's entry to the chemical industry by selling compounds produced by the OHD process.

Dr Seddon will also help define what further processing is needed to manufacture commodity chemicals. His initial report is attached to this report. Most of our work to date has used Victorian Brown Coal (VBC) as feedstock, while some trials have been done with Collie Coal (CC). In all cases the OHD reactor has performed faultlessly.

Greenpower Energy is also developing plans to build processing plants in Victoria to treat VBC and Western Australia to treat Collie Coal. The first plants will be small commercial demonstration units designed to treat 20 tonnes of coal per day and will initially focus on producing agricultural biostimulants. One of the plants will be completed to the stage where the OHD compounds can be produced as solids. This plant will form part of a demonstration facility for a large scale commodity chemical plant.

Information brochures describing the technical aspects of OHD operations at Collie and Gippsland have been compiled, and are included later in this report.

#### **Bio-Diesel Fuels**

The raw OHD liquor is an excellent feedstock for moulds and fungi. At present no systematic investigations have been made, other than the qualitative observation that submerged lipid bearing cultures are readily formed in the OHD liquor. We plan to react these lipids with an alcohol (ethanol or methanol) to form fatty acid methyl esters — or FAMEs. A deeper investigation of the biodiesel potential of the OHD liquor will be undertaken at Monash University by the same researchers currently working on agricultural biostimulants.

#### Licence Acquisition

Greenpower Energy's partnership with US company Thermaquatica is progressing well. All the payments due under the Research & Option Agreement to Thermaquatica from Greenpower have now been made, following a final payment of \$US244,000. We have commenced negotiating the detailed terms of the Exclusive License to use the OHD technology, and expect to complete and sign the License during May.

Executive Director Gerard King said, "I'm delighted to be part of a project that may substantially help our farmers and horticulturalists. Our biostimulants will promote plant health and, in the long term, will increase carbon-in-soil levels. Just as exciting is the prospect of Greenpower's entry to the international chemical market, by turning coal into commodity chemicals. We believe we will be able to do this at prices that will compete successfully with chemicals derived from petroleum.

"We are also optimistic about using the fungus/mould growing properties of the OHD liquor to produce biodiesel at a competitive cost."

#### About the OHD process:

The OHD process converts carbonaceous material into organic compounds. The scientific basis of the process is described and elaborated in USA Patent PCT/210/0233886, dated August 19, 2010.

When applied to VBC the relative simplicity of the process in combination with the highly reactive coal enables organic compounds to be made on an economically favourable basis. Processing of 1 tonne of VBC will yield ~400kg of organic compounds. On a per tonne of ROM VBC basis the input costs are less than \$100 (coal, oxygen, electricity & labour). The OHD process does not require complex machinery and for a small plant of 20 tonnes/day the capital intensity is less than \$1 million per daily tonne of product.

#### About plant biostimulants:

The accelerated use of biostimulants in agriculture is a recent phenomenon. In a major study Calvo, Nelson & Kloepper [ <a href="http://link.springer.com/article/10.1007%2FS11104-014-2131-8#page-1">http://link.springer.com/article/10.1007%2FS11104-014-2131-8#page-1</a> ] conclude: "Plant biostimulants are diverse substances and microorganisms used to enhance plant growth. The global market for biostimulants is projected to increase 12% per year and reach \$2200 million by 2018." Biostimulants are a varied group and one major group is "humic substances" of which fulvic acid is itself a major component. Humic substances comprise a contiguous family of substances ranging from humic acid (high molecular weight and brown) to fulvic acid (low molecular weight and yellow). Figure 2 above shows this relationship.

#### About biodiesel:

Biodiesel is made by chemically reacting lipids with an alcohol (ethyl alcohol or methyl alcohol). This product can be used in standard diesel engines—modifications are not required and it can be used alone or blended with petro diesel in any proportions. Biodiesel should not be confused with the usage of vegetable and waste oils that require modification to standard diesel engines. Wikipedia on line encyclopaedia contains a good article (22 pages) on biodiesel that is easy to understand for the general reader.

## **NEW INDUSTRY FOR COLLIE**

Serving the agricultural industry Becoming a part of an international industry



## **Conversion of Coal to Chemicals**

# **Our Project**

- One of the few processes which converts coal to useful products without greenhouse gas discharge.
- Requires coal, water electricity and liquid oxygen-nothing else.
- Called OHD [Oxidative Hydrothermal Dissolution].
- An oxidative process. The primary output contains no hydrocarbons.
- The basic output liquid is an agricultural biostimulant.
- Basic output contains a number of valuable speciality and fine chemicals.
- Basic output can be hydrogenated to make valuable high usage high value commodity chemicals.

### THE BASIC OUTPUT

An Agricultural Biostimulant.

The basic output is ~1.5% chemicals [in solution] and 98.5% water and simple reverse osmosis can bring that up to ~5.5% chemicals. In this form it can be applied to plants and have the same effect as the fulvic material as currently marketed.

Collie coal produces approximately 9000 litres of the "5.5%" liquid per tonne of ROM material.

Usage of agricultural biostimulants is estimated to increase [on a world wide basis] by 12% per annum over the next 4 years ["BIOSTIMULANTS MARKET: GLOBAL TRENDS & FORECASTS TO 2019: www.marketsandmarkets.com]. At present fulvic material is regarded as a high priced material and its usage is restricted to the high yield end of

agriculture: fruit flowers and vegetables. Our product can be produced at a much reduced cost base and on economic grounds will put fulvic material within reach of the broad acre farmers.

chemicals and specialty chemicals. The table [overleaf] lists the individual chemicals which result from OHD conversion of Collie Coal. Some of the listed chemicals such as CAS-19438-10-9 have a specialised use. Demand is like likely to be limited. For this chemical the information organization, "Molbase" quotes a reference price of \$153/kg. The "Molbase" reference price tends to be a median derived value.

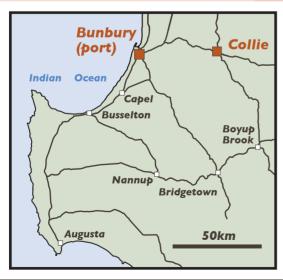
Commodity Chemicals: Most of the Collie Coal products can, by a process of hydrogenation be converted to one or more of the so called "commodity chemicals". Commodity chemicals are produced on a very large scale to satisy the demand from the global chemistry industry. For example the annual world production of benzene is over 20 million tonnes. Currently most of this is derived from hydrocarbon sources and its selling price is a function of crude oil prices. For instance if crude is \$35/bbl then benzene will sell for +/-\$514/tonne.

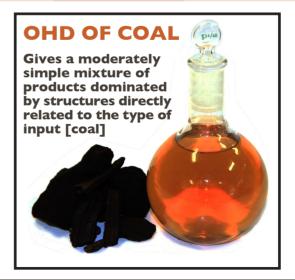
Hydrogenation of the Collie Coal OHD product will produce BTX commodity chemicals [benzene, toluene, xylenes], C9 & C10 aromatics and naphtha. For prices derived from a USD\$35/bbl reference a tonne of Collie coal will produce chemicals with a sale price of \$171/tonne. For crude at \$50 tonne the value rises to \$221/tonne.

# Products from Collie Coal



Compound	% of total	CAS No	Use	Reduced Product
Anisole (methoxybenzene □	<i>1.</i> 75□	<i>00-66-3</i> $\square$	Octane booster	Benzene
Methyl 3-methoxybenzoate (mHB) □	12.83	5368-81-0 <b></b>		Toluene
Methyl 4-methoxybenzoate (pHB) □	7.18	121-98-2 📖	]	Toluene
Dimethyl Terephthalate □	1.61	120-61-6	Chemical Intermediate (very large) □	p-Xylene
Dimethyl isophthalate IIII	4.36	1459-93-4	Plasticiser □ □	m-Xylene
6,7-Dimethoxy-m-cymene Ⅲ	1.07			m-cymene
Methyl 3hydroxybenzoate:				
m-Carbomethoxyphenol Ⅲ	4.79	19438-10-9	Medicinal□	Toluene
Methyl 3,5-Dimethoxy benzoate ☐	4.84	<i>5081-39-4</i> □	Flavour, perfume □	Toluene
Methyl 3,4-Dimethoxy benzoate ☐	2.42	2150-38-1	Flavour, perfume □	Toluene
Unassigned?	2.43			
Dimethyl 2-Hydroxy Terephthalate□	7.63	6342-72-9		p-Xylene
C3 alkyl hydoxy methoxy benzoate	5.82			Toluene
(unknown isomer)□				
1,7,7-trimethyl-2(1H)-Naphthalelenone,				
octahydro-4A-(hydroxymethyl)*□	9.81			Decalin
C16 FAME (as methyl palmitate ☐	1.74	112-39-0	Flavour, biodiesel□	n-Hexadecane (cetane)
Dimethyl 4-Methoxy				
Terephthalate;Dimethyl 2-				
methoxyterephthalate III	1.93			p-Xylene
Trimethyl trimellitate (1,2,4				
Benzenetricarboxylic acid trimethyl ester)		2459 101 🗆	Plasticiser (auto) □	pseuo-Cumene
Trimethyl trimesate IIII	28.15	2672-58-4	Plasticiser III	Benzene
Unassigned?				





## RENEWALL FOR LATROBE VALLEY

Serving the agricultural industry
Becoming a part of an international industry



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agriculture: fruit flowers and vegetables. Our product can be produced at a much reduced cost base and on economic grounds will put fulvic material within reach of the broad acre farmers.

chemicals. The table [overleaf] lists the individual chemicals which result from OHD conversion of VBC. Some of the listed chemicals such as CAS-1732-10-1 have a specialised use. For this chemical the information organization, "Molbase" quotes a reference price of \$125/kg. The "Molbase" reference price tends to be a median derived value.

Commodity Chemicals: Most of the VBC products can, by a process of hydrogenation be converted to one or more of the so called "commodity chemicals". Commodity chemicals are produced on a very large scale to satisy the demand from the global chemistry industry. For example the annual world production of benzene is over 20 million tonnes. Currently most of this is derived from hydrocarbon sources and its selling price is a function of crude oil prices. For instance if crude is \$35/bbl then benzene will sell for +/- \$514/tonne.

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# Products from Victorian Brown Coal (VBC)



Compound	% of total	CAS No	<i>U</i> se	Reduced Product
Anisole	2.09	100-66-3	Octane Booster	Benzene
Dimethyl Succinate	2.44	100-65-0	Food additive;flavourin	Butane
Dimethyl, 2-Methyl succinate	0.87	1604-11-1	Food additive;flavouring	2-methylbutane
Methyl Benzoate	0.68	93-58-3	Fragrance	Toluene
Methoxy phenol; Guaiacol	0.58	150-76-5	Fragrance;antisceptic	Benzene
1,2-Dimethoxybenzene; veratrol	6.43	91-16-7		Benzene
1,3-Dimethoxybenzene	0.79	151-10-0		Benzene
1,4-Dimethoxybenzene	1.99	150-78-7		Benzene
4-Methoxy Benzaldehyde	1.65	123-11-5	Fragrance [large use]	Toluene
Trimethoxybenzene	1.94	135-77-3		Benzene
Methyl 3-Methoxybenzoate	2.85	5638-81-0		Toluene
Dimethyl Pimelate	0.56	1732-08-7		n-Heptane
Methyl 2-Methoxybenzoate	0.56	606-45-1	Flavouring	Toluene
1,2,4-Trimethoxybenzene	1.16	135-77-3	· ·	Benzene
Methyl 4-Methoxybenzoate	12.29	121-98-2		Toluene
3-Methoxy Acetophenone	1.01	586-37-8		Ethylbenzene
Methyl 3-methoxy-4-methylbenzoate	0.65	3556-83-0	Flavouring	p-Xylene
Trimethoxybenzene	1.25	14107-97-2	Flavouring	Benzene
Dimethyl suberate	1.34	1732-09-8		n-Octane
Trimethoxytoluene	1.27	14107-97-2		Toluene
Dimethyl azelate	1.49	1732-10-1	cosmetics;grease	n-noname
3,4-dimethoxybenzaldehyde	5.21	120-14-9	Flavouring; Oderant	Toluene
Methyl Vanillate	0.77	3943-74-6	Flavouring	Toluene
Methyl 3,5-Dimethoxybenzoate	4.03	25081-39-4	Flavouring; perfume	Toluene
Methyl veratrate	24.8	2150-38-1	Flavouring; perfume	Toluene
2,4-Dimethoxyacetaphenone	3.03	829-20-9	<u> </u>	Xylene
Possibly dimethyl phthalate	1.17	131-11-3		
Dimethyl Sebacate	0.76	106-79-6	Platiciser, cosmetics	n-Decane
Unasigned	1.49			
3,4,5-trimethoxybenzaldehyde	1.2	86-81-7	Pharma. Intermediate	Toluene
Methyl 3,4,5-trimethoxybenzoate	4.1	1916-07-0	Fragrance	Toluene
•	1.55			
	3.24			
Methyl Palmitate	0.87	112-39-0	Flavour, biodiesel	n-hexadecane
Dimethyl 4-methoxyterephthalate	0.8	120-61-6		Benzene
	0.72			
	0.81			
Trimethyl 1,3,5-benzenetricarboxylate	0.75	2672-58-4		Benzene
	0.82			





# REPORT AND COMMENTARY ON

# COAL TO CHEMICALS WITH REFERENCE TO

# OXYGENATED PRODUCTS PRODUCED FROM THE OXIDATIVE HYDROTHERMAL DISSOLUTION OF VICTORIAN BROWN COAL AND COLLIE COAL

#### **FOR**

#### **GREENPOWER ENERGY LTD**

DR. DUNCAN SEDDON FRACI, CChem

**APRIL 7, 2016** 

**DUNCAN SEDDON & ASSOCIATES PTY. LTD.** 

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#### **BACKGROUND**

GreenPower Energy Ltd. has an interest in technology for converting coal into chemicals. Of particular interest is the Oxidative Hydrothermal Dissolution (OHD) process under development and promoted by Professor Ken Anderson of Thermaquatica Inc. and the University of Southern Illinois.

GreenPower Energy has provided Duncan Seddon & Associates with preliminary results of OHD conversion of Victorian Brown Coal and Collie Coal from Western Australia. The key features of the material provided are an analysis of the OHD products from the two coals and a report concerning the possible scope of a conversion process based on Victorian Brown Coal. This report indicates that *prima facie* that the OHD process coverts the coal completely and that all products can be accounted for.

GreenPower Energy has commissioned Duncan Seddon & Associates to provide advice relating to the value of the products of OHD and how the products could be transformed into materials of interest to the chemicals and fuels industry at large. This report addresses these issues based on the information provided.

#### **CAVEATS**

The report provided is based on the limited amount of data provided. In due course other data may come into the possession of Duncan Seddon & Associates which could materially influence the analysis provided, the conclusions and the recommendations made in this report.

Duncan Seddon and Associates has lengthy experience in industrial chemicals business, particularly in the field of "commodity chemicals" and fuels. Many of the products of the OHD process could find a role in the fields of "fine chemicals" and "speciality chemicals". It will be realised that these are specialist fields and conclusions and recommendations for these uses may be revised in the light of further information and research.

Similarly the conversion of the OHD products to commodity chemicals requires technological solutions that are not yet defined and commercial processes may require some development to make them suitable for OHD products. Again conclusions and recommendations may be revised in the light of further information and research.

Given these caveats, Duncan Seddon and Associates has used best endeavours to identify the value of the OHD products and to identify how the products could be transformed to materials of interest to the chemicals and fuels industry at large.

#### UNLESS OTHERWISE INDICATED ALL PRICES ARE IN US DOLLARS

#### **SUMMARY**

The OHD process converts coal into compounds containing the elements carbon, hydrogen and oxygen (oxygenates). Many of these oxygenates contain a single aromatic ring. *Pima facie* there are no poly-nuclear aromatic compounds. A smaller portion of the oxygenates are produced as esters of di-carboxylic acids. These are more prevalent in the product spectrum of Victorian brown coal than in the products from Collie coal.

There are notably fewer products from Collie coal than Victorian brown coal and *prima facie* these could be separated and purified by vacuum distillation and, as may be necessary, fractional crystallisation.

#### **Speciality and Fine Chemicals Market**

Several of the products are of interest to the speciality chemicals and fine chemicals market. Such products would have high sales value but total demand would be small. However, the bulk of the products do not appear to be of immediate interest. This may be because of the unique nature of many OHD products and more applications in the speciality and fine chemicals market might be found should pure samples become available for potential users to evaluate.

It may be feasible to develop a small business enterprise refining and selling coal OHD products to the speciality and fine chemicals market using OHD products from a demonstration plant constructed to help commercialise the large scale conversion of coal using the OHD process.

#### **Commodity Chemicals and Fuels**

Only a small part of the total product fraction produced are of immediate use in the commodity (bulk) chemicals and fuels market. For a large scale coal OHD enterprise, the bulk of the products would require transforming into products of interest.

There is a lack of suitable technology for restructuring the primary OHD oxygenates, either by isomerisation or selective partial hydrogenation. *Prima facie* the best option would be to remove the oxygen by hydrogenation with a selective technology which would preserve the aromatic ring. This route minimises hydrogen demand and maximises value in the hydrocarbon products produced. All products (BTX and naphtha) are easily sold on the large international bulk chemicals markets.

#### **Greenfields Development**

A possible greenfield development based on Collie coal would have the features shown in the table. Only coal is required as input with oxygen and hydrogen being produced within the site boundary. Coal use could fall by 1.6 million tonnes should natural gas be available for the production of hydrogen.

Collie coal input	Mt/y	2.61
Coal gross calorific value (HHV)	GJ/t	18.2
Yield of hydrocarbons (as % of C and H present in coal)		80%
Benzene	kt/y	75
Toluene	kt/y	150
Xylenes (including ethylbenzene)	kt/y	60.4
C9 and C10 aromatics	kt/y	11.4
Naphtha	kt/y	99.9
Process thermal efficiency	%	35.5%

Such a scheme would be sensitive to the prevailing price of crude oil. With oil at \$35/bbl the facility would have the following statistics:

Input coal cost		\$/tonne coal	\$30.0
Total coal cost		\$M/y	\$78.2
Benzene	\$514.6/t	\$M/y	38.6
Toluene	\$439.1/t	\$M/y	65.9
Xylenes (including ethylbenzene)	\$477.4/t	\$M/y	28.8
C9 and C10 aromatics	\$439.1/t	\$M/y	5.0
Naphtha	\$318.8/t	\$M/y	31.9
Total Revenue		\$M/y	170.95
Cash Margin		\$M/y	91.95

Based on crude oil price of \$35/bbl, these statistics give a revenue of \$171 million/year as shown in Table. This results in a cash margin of \$92/million/year. The process is very sensitive to the prevailing oil price. With oil at \$50/bbl revenue jumps to \$223 million/year and the gross cash margin to \$145 million/year.

#### COAL TO CHEMICALS BY OHD PROCESS

#### Overview

In essence, the Oxidative Hydrothermal Dissolution Process (OHD) involves the partial oxidation of coal held at high pressure in sub-critical water. The partial oxidation products are soluble in the water phase.

In general, the products comprise two broad classes:

1. Alpha and omega oxygenated liner paraffins (alkanes) as acids or esters such as dimethyl suberate; Figure 1:

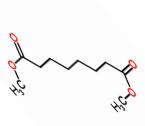


Figure 1: Dimethyl suberate produced from Victorian Brown Coal

These materials are produced in small quantities (less than 5% of total) in the products of Victorian Brown Coal and may be present in trace quantities in the Collie Coal .

2. Oxygenated mononuclear aromatics containing methoxy, hydroxyl, aldehyde acids or ester groups such as dimethyl 2-methoxyterephthalate; Figure 2.

Figure 2: Dimethyl 2-methoxyterephthalate produced from both Victorian Brown Coal and Collie Coal

Compounds in this class are the most common with some individual compounds found in high concentrations in the product.

The product spectrum from two coals are considered separately, namely Victorian Brown Coal (VBC) and Collie Coal. VBC product spectrum is more complex and contains more identified compounds than the Collie coal product spectrum.

The object of this report to identify uses for the products or determine how the individual products may be converted into chemicals of significance

#### **Victorian Brown Coal Products**

The product spectrum of the VBC comprises 39 species of which 33 are identified comprising over 90% of the product. Six products are unidentified comprising 9.8% of the products. The products are listed in Table 1.

The products have been separated by chromatography and the first column gives the elution peak number and the second column the percentage (weight) in the product. This data was provided by GreenPower Energy and so acts as a cross check for the compounds discussed.

The third column gives the common name of the compound as used by the Royal Chemical Society website *ChemSpider*<sup>1</sup>, some of these have been changed from the original data. Common alternatives are included. To ease visualisation of the structure of some of the more significant compounds are illustrated in Appendix 2; diagrams from *ChemSpider*.

The forth column gives the *Chemical Abstract Number* (CAS#). Some of the compounds in the list have alternative CAS numbers; these have not been included.

<sup>&</sup>lt;sup>1</sup> ChemSpider: www.chemspider.com

The fifth column gives the compound molecular weight (MW).

The sixth column gives the typical use of the pure compound where a use has been identified. Because many of the compounds are rare, a blank in this column should not be interpreted as being of no interest to the fine chemicals business (cosmetic, flavouring medicinal etc.) rather the rarity may have prevented evaluation of the compound.

Of the uses identified, most are in the fine chemicals business (food additives, flavourings, cosmetics and perfume) with total world demand in a few hundred tonnes at most and with typical shipments in the kilograms or less. Inspection of current quotes indicates a price of typically \$60/kg of >99% purity product. The largest demand is probably for 4-methoxy benzaldehyde (Pk 9 which is less than 2% of the total products) which seems to have a large demand as a fragrance additive.

Of the commodity chemicals, anisole (Pk 1; 2% of the product slate) has been proposed (but not widely used) as an octane booster. Dimethyl sebacate (Pk 28; <1% of product slate is used as a plasticiser for cellulosic resins.

The seventh and eight column gives the melting and normal boiling points as reported by *ChemSpider*. For high boiling materials (b.p. >270°C) this is often by predictive algorithms with most high boiling materials being distilled under vacuum.

The ninth and final column gives the end product of reduction assuming aromatic nucleus is held intact.

Table 1: Products from Victorian Brown Coal

Pk.	% of total	COMPOUND	CAS#	MW	USE	Мр	Вр	REDUCED
						(°C)	(°C)	PRODUCT
1	2.09%	Anisole	100-66-3	108.1	Octane booster	-37	154	Benzene
2	2.44%	Dimethyl Succinate	106-65-0	146.1	Food additive, flavouring	19	196	Butane
3	0.87%	Dimethyl, 2-Methyl succinate	1604-11-1	160.2	Food additive, flavouring		196	2-Methylbutane (isopentane)
4	0.68%	Methyl Benzoate	93-58-3	136.1	Fragrance	-12	199	Toluene
5	0.58%	Methoxy phenol (probably 2 methoxy isomer); Guaiacol	150-76-5	124.1	fragrance, antisceptic	28	205	Benzene
6	6.43%	1,2-Dimethoxybenzene; veratrol	91-16-7	138.16		22	206	Benzene
7	0.79%	1,3-Dimethoxybenzene	151-10-0	138.16		-52	217	Benzene
8	1.99%	1,4-Dimethoxybenzene	150-78-7	138.16		56	213	Benzene
9	1.65%	4-Methoxy Benzaldehyde; 4-Anisaldehyde	123-11-5	136.1	Fragrance (large use)	0	248	Toluene
10	1.94%	Trimethoxybenzene (probably 1,2,3 isomer)	135-77-3	168.19		45	241	Benzene
11	2.85%	Methyl 3-Methoxybenzoate	5368-81-0	166.2			238	Toluene
12	0.56%	Dimethyl Pimelate; 10V5V01	1732-08-7	188.2		-21	250	n-Heptane
13	0.56%	Methyl 2-Methoxybenzoate	606-45-1	166.2	Food flavouring		247	Toluene
14	1.16%	1,2,4-Trimethoxybenzene	135-77-3	168.2		52	247	Benzene
15	12.29%	Methyl 4-Methoxybenzoate (Methylated parahydroxy benzoic acid)	121-98-2	166.2		49	245	Toluene
16	1.01%	3-Methoxy Acetophenone	586-37-8	150.2		-7	240	Ethylbenzene
17	0.65%	Methyl 3-methoxy-4-methylbenzoate	3556-83-0	180.2	Flavouring	46	257	p-Xylene
18	1.25%	Trimethoxybenzene (probably 1,3,5 isomer)	14107-97-2	168.2	Flavouring	51	255	Benzene
19	1.34%	Dimethyl suberate	1732-09-8	202.2		-3	267	n-Octane
20	1.27%	Trimethoxytoluene (probably 2,4,6 isomer);	14107-97-2	182.2		28	292	Toluene
		1,3,5-Trimethoxy-2-methylbenzene						
21	1.49%	Dimethyl azelate	1732-10-1	216.3	Cosmetic/ Li Grease	18	276	n-Nonane
22	5.21%	3,4-dimethoxybenzaldehyde; veratraldehyde	120-14-9	166.2	Flavoring, oderant	44	281	Toluene
23	0.77%	Methyl vanillate	3943-74-6	182.1	Flavouring	65	286	Toluene
24	4.03%	Methyl 3,5-Dimethoxybenzoate (isomer of peak 25)	25081-39-4	196.2	Flavour, perfume	42	298	Toluene
25	24.80%	Methyl veratrate (Methyl 3,4-	2150-38-1	196.2	Flavour, perfume	60	283	Toluene
					•			

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		dimethoxybenzoate)						
26	3.03%	2,4-Dimethoxyacetophenone	829-20-9	180.2		40	288	Xylene
27	1.17%	Unassigned (possibly dimethyl phthalate)	131-11-3					
28	0.76%	Dimethyl Sebacate	106-79-6	230.3	Plasticiser (cellulosic resins), cosmetics	27	288	n-Decane
29	1.49%	Unassigned						
30	1.20%	3,4,5-Trimethoxybenzaldehyde	86-81-7	196.2	Pharmaceutical intermediate	75	311	Toluene
31	4.10%	Methyl 3,4,5-trimethoxybenzoate	1916-07-0	226.2	Fragrance	84	274	Toluene
32	1.55%	Unassigned						
33	3.24%	Unassigned						
34	0.87%	Methyl Palmitate	112-39-0	270.2	Flavouring, biodiesel	30	332	n-Hexadecane (cetane)
35	0.80%	Dimethyl 4-methoxyterephthalate	120-61-6					Benzene
36	0.72%	Unassigned						
37	0.81%	Unassigned						
38	0.75%	Trimethyl 1,3,5-benzenetricarboxylate; trimethyltrimesate	2672-58-4	252.2		146		Benzene
39	0.82%	unassigned						
	9.80%	Total unassigned	unknown	236				
	100.00%							

#### **Collie Coal Products**

The Collie Coal product slate comprises 17 product of which 16 are identified. The products are listed in Table 2 which is similar to Table 1 for VBC.

The products have been separated by chromatography and the first column gives the elution peak number and the second column the percentage (weight) in the product. This data was provided by GreenPower Energy and so acts as a cross check for the compounds discussed.

The third column gives the common name of the compound as used by the Royal Chemical Society website *ChemSpider*, some of these have been changed from the original data. Common alternatives are included. To ease visualisation of the structure some of the more significant compounds are illustrated in Appendix 2; diagrams from *ChemSpider*. Some of the Collie Coal products have not been definitively identified and several isomers are possible. Of particular note are Pk 13, a naphthalone derivative (nearly 10% of the product slate), Pk 12 (isomer to a C3 alkyl hydroxy methoxy benzoate (nearly 6% of the product slate).

The fourth column gives the Chemical Abstract Number (CAS#). Some of the compounds in the list have alternative CAS numbers. These have not been included. Because some of the compounds are not defined, the CAS number cannot be assigned. For Pk 15 Dimethyl 2-methoxy terephthalate the CAS number is unknown. Note that this compound is named dimethyl 4-methoxy terephthalate in the original data which cannot be correct.

The fifth column gives the compound molecular weight (MW).

The sixth column gives the typical use of the pure compound where a use has been identified. As before, because many of the compounds are rare, a blank in this column should not be interpreted as being of no interest to the fine chemicals business (cosmetic, flavouring medicinal etc.) rather the rarity may have prevented evaluation of the compound.

Of the uses identified, some are in the fine chemicals business (food additives, flavourings, cosmetics and perfume) with total world demand in a few hundred tonnes at most and with typical shipments in the kilograms or less. Inspection of current quotes indicates a price of typically \$60/kg of >99% purity product.

Of the commodity chemicals, anisole (Pk 1; 2% of the product slate) has been proposed (but not widely used) as an octane booster. Dimethyl terephthalate (Pk 4; <2% of product slate is a major commodity chemical and dimethyl isophthalate (Pk 5; ~4% of the product slate) is widely used as to produce plasticisers. Chemicals Pk 16 & 17 (30% of the product slate) are also widely used as plasticiser intermediates particularly for internal auto-plastics (vinyls) because of their very low vapour pressure (hence low smell).

The seventh and eight column gives the melting and normal boiling points as reported by *ChemSpider*. For high boiling materials (b.p. >270°C) this is often by predictive algorithms with most high boiling materials being distilled under vacuum.

The ninth and final column gives the end product of reduction assuming aromatic nucleus is held intact.

Table 2: Products from Collie Coal

Pk	% of	COMPOUND	CAS No	MW	USE	Mp	bp	REDUCED
	total					(°C)	(°C)	PRODUCT
1	1.75%	Anisole (Methoxybenzene)	100-66-3	108.1	Octane booster	-37	154	Benzene
2	12.83%	Methyl 3-methoxybenzoate (mHB)	5368-81-0	166.2			238	Toluene
3	7.18%	Methyl 4-methoxybenzoate (pHB)	121-98-2	166.2		49	245	Toluene
4	1.61%	Dimethyl Terephthalate	120-61-6	194.18	Pet Chem intermediate	141	288	p-Xylene
					(very large)			
5	4.36%	Dimethyl isophthalate	1459-93-4	194.18	Pet Chem intermediate (for	68	282	m-Xylene
					plasticiser)			
6	1.07%	6,7-Dimethoxy-m-cymene (?)		194.3			247	m-Cymene
7	4.79%	Methyl 3-hydroxybenzoate; m-	19438-10-9	152.1	Medicinal	73	280	Toluene
		Carbomethoxyphenol						
8	4.84%	Methyl 3,5-Dimethoxy benzoate	25081-39-4	196.2	Flavour, perfume	42	298	Toluene
9	2.42%	Methyl 3,4-Dimethoxy benzoate	2150-38-1	196.2	Flavour, perfume	60	283	Toluene
10	2.43%	Unassigned (?)						
11	7.63%	Dimethyl 2-Hydroxy Terephthalate	6342-72-9	210.2			327.6	p-Xylene
12	5.82%	C3 alkyl hydroxy methoxy benzoate (unknown	unknown	210.2				Toluene
		isomer)						
13	9.81%	1,7,7-trimethyl-2(1H)-Naphthalenone, octahydro-	unknown	194.3				Decalin
		4A-(hydroxymethyl)- (*)						
14	1.74%	C16 FAME (as methyl palmitate)	112-39-0	270.2	Flavoring, biodiesel	30	332	n-Hexadecane
								(cetane)
15	1.93%	Dimethyl 4-Methoxy Terephthalate; Dimethyl 2-	unknown	224.2				p-Xylene
		methoxyterephthalate						
16	1.64%	Trimethyl trimellitate (1,2,4-Benzenetricarboxylic	2459-10-1	252.2	Plasticiser (auto uses)	39	338	pseuo-Cumene
		acid trimethyl ester)						
17	28.15%	Trimethyl trimesate (1,3,5-Benzenetricarboxylic	2672-58-4	252.2	Plasticiser ? (auto uses)	146		Benzene
		acid, trimethyl ester)						
		Unassigned (?)		196				Unassigned
	100.00%							

#### **CHEMICALS MARKET**

As illustrated in Tables 1 & 2, all the products of coal OHD, are volatile with boiling points below 350°C. This is typical of the top boiling components for automotive diesel and below the boiling points of vacuum gas oils used to produce lubricating oil. In theory the products, especially for the Collie coal products which are fewer in number, could be separated by distillation either at atmospheric pressure or, if necessary to prevent decomposition, distillation *in vacuo*. Again, in theory, fractional crystallisation could separate materials with similar boiling points. In this manner each of the components could be separated and purified for sale.

The market for chemicals can be usefully divided into several sectors and coal OHD products could find application these sectors. These are discussed below:

#### **Fine Chemicals**

This market concerns the supply of chemicals to high value industries for the manufacture of pharmaceuticals, cosmetics, flavourings and agriculturally active chemicals such as insecticides and fungicides. Often the chemicals are intermediates in the production of a final product or represent only one component in the final product. For the most part a purchaser is not necessarily tied to a specific chemical or intermediate for he usually has alternative strategies of achieving his desired final outcome.

#### **Pricing**

The fine chemicals market is a high unit value market but products must be made to exacting purity standards (typically >99%) and packaging costs are high. Typical world production of a fine chemical is less than 1000t/y and prices over \$US10/kg. Pricing is largely independent of the rise and fall of prices in the general commodity chemicals markets. However, pricing of individual compound is vague since there is no open market other than quotations from suppliers.

Most fine chemicals are produced in batches from purified starting compounds. Often multiple stages are required. This leads to high production costs. Large scale production of a specific fine chemical by the OHD process may undermine the pricing structure of the chemical or series of chemicals. This will have to be considered in the development process.

#### **Players**

There are several international players who specialise in marketing fine chemicals. Often these players are also involved in producing products. *Wikipedia* lists the following fine chemicals companies (Table 3).

Table 3: Major fine chemicals companies (figures are the *Wikipedia* authors estimates)

	Company	Location	Sales 2009	Fine Chemical	Sales 2009
			(\$ million)	unit	(\$ million)
1	Lonza	Switzerland	2600	Custom. Manuf.	1370
2	Boehringer-Ingelheim	Germany	18300	Fine Chem.	950
3	DSM	The Netherlands	11300	Fine Chem	850
4	Sumitomo Chemicals	Japan	17420	Fine Chem.	730
5	Merck KGaA	Germany	11200	Life Science	580
				Solutions	
6	Sigma-Aldrich	USA	2148	SAFC	570
7	BASF	Germany	73000	Fine Chem.	550
8	CSPC Shijiazhuang	China	1500	Fine Chem.	550
	Pharmaceutical Group				
9	Lanxess	Germany	7280	Saltigo	550
10	Albemarle	USA	2005	Fine Chem.	500

#### Accessing the Market

The major portion of the primary products of the Collie Coal OHD product slate could be regarded as falling into the fine chemicals class. The route for coal OHD products to access the fine chemicals market would require:

- 1. The construction of suitable OHD process plant that could repeatedly reproduce the same product slate and be of a size capable of producing kilogram quantities of material. Such a facility could be a pilot of demonstration facility for a larger coal OHD venture.
- 2. Separation of the product into the individual compounds. This could be accomplished by vacuum distillation or crystallisation or a combination of these processes.
- 3. Further purification as may be necessary to the required purity required for the fine chemical in question and provision of samples to prospective purchasers.
- 4. Discussion with a suitable player or more probably players for suitable off-take agreements.

#### **Speciality Chemicals**

Speciality chemicals cover a wide range of chemical products from adhesives to additives for plastics, food, cosmetics and industrial cleaners. These chemicals are often referred to as effect chemicals or performance chemicals as they induce effects in other materials comprising the final product. Speciality chemicals may only have one or two uses. The unit demand for speciality chemicals is higher than for fine chemicals and some are used in 10,000t/y and more

amounts. Speciality chemicals make up most of the number of different chemicals used in commerce.

#### **Pricing**

There is no open market for speciality chemicals so pricing is vague. Generally prices fall in the US\$ 3 to 5/kg range (US\$3,000 - 5,000/t).

#### **Players**

There are many companies producing speciality chemicals and many are represented by various industry associations, for instance the British Association of Chemical Specialities (BACS). Wikipedia lists the following companies in the specialities field (Table 4):

Table 4: Major EU and US speciality chemicals companies

EU	USA
BASF	Huntsman
Akso Nobel	Ashland
Clarient	Chemtura
Evonik	Rockwood
Cognis	Albemarle
Kemira	Cabot
Lanxess	W.R. Grace
Rhodia	Ferro Corporation
Wacker	Cytec Industries
Croda	Lubrizol

#### Accessing the Market

The major portion of the primary products of the Collie Coal OHD product slate could be useful precursors for the production of speciality chemicals. For instance product 17 - trimethyl trimisate - which is nearly 30% of the OHD product could by trans-esterification with 2-ethylhexanol and used to produce a plasticiser for automobile vinyls.

The route for coal OHD products to access the speciality chemicals market would follow the similar route as that described for fine chemicals. Purification to the exacting standards for fine chemicals may not be required but kilogram samples of product made to a consistent quality would be required by prospective purchasers for evaluation.

An approach to a suitable player could be usefully made through one of the trade associations for speciality chemicals.

#### **Commodity Chemicals**

Commodity chemicals are produced on a very large scale to satisfy the global chemical industry. For example the annual world production of benzene is over 20 million tonnes. Commodity chemicals are produced in large integrated chemical complexes. Most is used internally within the complex to produce downstream chemicals (e.g. styrene) or final commodity products (e.g. polystyrene).

#### Pricing

There is a large trade in commodity chemicals between the various players in the industry. For most commodity chemicals there is an active spot market trading parcels of 1,000t of material or more depending on the commodity. Contract pricing is also reported and compared to spot pricing. There is a large international shipping fleet facilitating trans-oceanic trade of any commodity chemical.

Spot, contract prices, traded volumes, shipping details and shipping costs are reported by specialist agencies such as. ICIS LORS, Argus, Platts. These reporting agencies provide market data and commentary on a daily basis for many commodity chemicals.

The transparency and open nature of the market, more or less, results in similar prices for a given commodity chemical across the world. In a similar manner to the oil market, specialist traders quickly exploit any regional price differentials.

Prices are influenced by the prevailing price of crude oil which is the primary source for most commodity chemicals. Generally commodity chemicals sell at a healthy premium to transport fuels such as gasoline (petrol) or motor diesel fuel.

As discussed below one option to develop the coal OHD technology is to convert the oxygenate intermediates to aromatics - benzene, toluene and xylene (BTX). These chemical intermediates sell at a premium to gasoline. The correlation of BTX prices and naphtha by-product prices with the prevailing price of crude oil (Brent) have been published by Duncan Seddon and Associates and are reproduced in the Appendix 1.

#### **Players**

The major chemical companies are well known - ExxonMobil, Shell, Dow, Du Pont, BASF etc.

#### Accessing the Market

For coal OHD products the major issue is generating enough volume for a viable parcel (cargo size). For BTX this is typically 10,000t or more. Most OHD products are not in the commodity chemicals league and those which are, are only produced as a small percentage of the total coal OHD product (e.g. Collie coal products 4 and 5 dimethyl terephthalate and isophthalate total only 6% of the product slate).

To access the commodity chemicals market would require the hydrogenation of the primary OHD products to produce aromatics (benzene, toluene and xylene, BTX) which could be traded.

Because BTX is so readily traded as individual components or as a mixture, although possibly useful, it would not be necessary to have an arrangement with another major player.

#### **CONVERSION STRATEGIES**

Inspection of the above Tables 1 & 2 indicates that the principal issue is the conversion of various hydroxy and methoxy benzene carboxylic acids.

As well as researching the standard industrial texts, I have conducted preliminary (non exhaustive) searches using the Elsevier's *Scopus* website for pertinent academic papers<sup>2</sup> and the US Patents Service for pertinent patents. The results of these searches are given below.

#### **Conversion to higher valued products**

Isomerisation is a key process in the value chain for producing isophthalic acid and terephthalic acid but this occurs with the hydrocarbon precursors (xylenes) rather than as the acid or ester stages. Technology for isomerising benzene carboxylic acids e.g. the isomerisation of isophthalic acid into terephthalic acid appears unknown.

Hydroxy, methoxy benzene carboxylic acids could be selectively hydrogenated to produce material of larger demand for sale. For example, Collie Coal Product 2: Methyl 3-methoxybenzoate, has no direct uses but could be converted to benzoic acid (annual demand ~700kt/y or phenol (annual demand >1Mt/y): Figure 3.

However, this requires very selective hydrogenation processes. Production of phenol requires the decarboxylation of the ester group and hydrolysis of the methoxy grouping to form phenol. Production of benzoic acid requires the selective hydrogenation of hydroxyl group leaving the carboxylate group intact and hydrolysis of the carboxylate ester to form benzoic acid. These selective operations are likely to require multiple steps and single step routes are not immediately apparent.

In the absence of selective single step routes it would appear the only viable technical approach to more valuable (saleable) products is reduction (deoxygenation) or decarboxylation (removal of CO<sub>2</sub> moieties) to form hydrocarbons. For example methyl 3-methoxybenzoate could be reduced to toluene (Figure 3).

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<sup>&</sup>lt;sup>2</sup> A paper by Mäki-Arvela, Päivi, Holmbom, Bjarne, Salmi, Tapio and Murzin, Dmitry Yu., 'Recent Progress in Synthesis of Fine and Specialty Chemicals from Wood and Other Biomass by Heterogeneous Catalytic Processes', Catalysis Reviews, 49:3, 197 - 340 concerns the principal wood products which are non-aromatic in nature - unsaturated fatty acids, cellulose, terpenes - and is not revelvent to the bulk of the coal OHD products. The manuscript was kindly provided to the author by Dimitry Murzin who is thanked for this.

Figure 3: Possible conversion scenarios for methyl 3-methoxybenzoate to phenol, benzoic acid or toluene

To produce hydrocarbons from the coal OHD products, there are several possible approaches which are simply illustrated in Figure 4. This illustrates the conversion to possible products resulting from the removal of an hydroxyl group using phenol as an example starting compound.

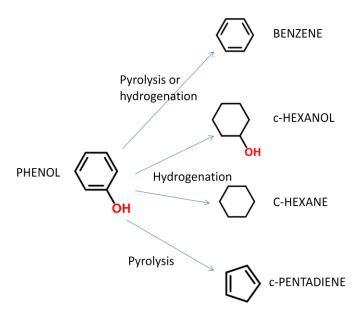


Figure 4. Possible conversion of an hydroxy-aromatic (phenol) into other products

#### Oxygen Removal by Pyrolysis

Conversion of the product slate by pyrolysis is feasible and this could be accomplished by heating the products, in the presence of steam which helps prevent coke formation, to high temperatures (800°C) for a short residence time (< 0.1 sec). This is the basis for large scale steam cracking of naphtha and gas oil to produce olefins (ethylene and propylene) and BTX coproducts.

Pyrolysis of the compounds of interest should effect oxygen removal, but the generally unselective free radical nature of the reactions would make the final products difficult to predict. Benzene (see Figure 4) would be a major product, but compounds containing hydroxy and methoxy side chains to the aromatic ring would also undergo CO elimination to form significant quantities of dienes such a *cyclo*-pentadiene. These dienes are by-products of naphtha and gas oil pyrolysis and are used to produce epoxy-resins but are not of particularly of high value.

Pyrolysis of the products from coal OHD is therefore not recommended.

#### Oxygen Removal by Catalytic Hydrogenation

Catalytic hydrogenation is far more selective than pyrolysis and could be used to produce valuable products from coal OHD products. Using phenol as the example compound (Figure 4) three products are possible - benzene, *cyclo*-hexanol or *cyclo*-hexane. Each of these compounds has significant commercial demand and value.

#### Cyclo-hexane

This is produced in large quantities by the reduction of benzene for the manufacture of polyamides - nylon 6 and nylon-66. However, reduction of the benzene ring will require not only large quantities of hydrogen for oxygenate removal but large quantities of hydrogen to complete the total reduction of the aromatic nucleus.

#### Cyclo-hexanol

The selective reduction of phenol to *cyclo*-hexanol is commercially practiced with the product used as a intermediate in the production of caprolactam, the key intermediate for the manufacture of nylon-6. This selective reduction is also heavily researched in the academic literature.

#### Benzene

Benzene would be the best option with major demand as an intermediate for the production of styrene and derivatives (polystyrene, styrene-butadiene-rubber) as well a polyamides. By keeping the aromatic ring intact the consumption of hydrogen would be limited to removal of the oxygenate side chains on coal OHD products.

#### Overview of Pertinent Commercial Catalytic Hydrogenation Technology

Catalytic hydrogenation is widespread in the chemical process industries and available in many forms from a wide range of process licensors. In broad terms there are two approaches (i) using transition metal catalysts (nickel, cobalt etc.) at relative high temperature and high pressure, and (ii) using noble metal catalysts (platinum, palladium) at low temperatures and low pressures. The former were developed by companies of the I.G. Farben group in the 1920s and 30s, whilst the latter were developed by US companies during the 1940s and 50s. Using platinum metals usually produces better selectivity but at higher catalyst cost. To some extent even today these historical differences are reflected in the approach of process licensors - European licensors generally offering technology based on transition metals and US licensors on noble metals.

#### Thermodynamic considerations

We are primarily concerned with hydrogenation reactions which would leave the aromatic nucleus remaining intact. Reduction of the aromatic ring or the conversion of a naphthene (*cyclo*-hexane) into an aromatic (benzene) is determined by the thermodynamic equilibrium. Low temperature reductions favour naphthenes and high temperatures favour aromatics. The cross-over temperature is in the range 400 to 500°C. Hydrogenation below this temperature range would lead naturally to saturation of the ring (to *cyclo*-hexane) whilst hydrogenation at higher temperatures would preserve the aromatic nucleus and promote aromatic formation from any naphthenes present.

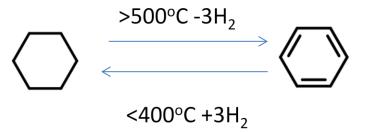


Figure 5: Cyclo-hexane-benzene conversion

There are several existing technologies that could be adapted for the conversion of coal OHD products.

#### Naphtha Reforming

This technology uses platinum supported on alumina catalysts for the conversion of naphtha (low octane, naphthene rich fraction of crude oil) into high octane aromatic blendstocks. This process is the main commercial process for producing aromatics for both octane blending in gasoline (petrol) and to produce aromatics (benzene, toluene and xylene; BTX) for the chemicals industry. Naphtha reforming is typically conducted at temperatures over 500°C with hydrogen at 100 bar pressure.

It would be expected that this technology could hydrogenate the coal OHD products. Furthermore, it would be expected that C6 and higher aliphatic molecules (hexane etc.), would be reformed into aromatics boosting the overall yield of aromatics from the coal OHD products. Its efficiency in removing the oxygenates moieties is less clear and would have to be evaluated.

A variant on this process (using a palladium catalysts at 300°C) has been adapted to produce *cyclo*-hexanol from phenol.

#### Fuel Hydro-treating

Oil refinery hydro-treaters have a range of duties from removing unsaturates (olefins etc) to removal of non hydrocarbon components particularly sulphur compounds but also nitrogen and oxygen compounds (phenol is reduced to benzene). Generally hydro-treaters operate at low temperature (270 - 340°C) so that aromatic rings are also hydrogenated. Hydro-treaters operate over a wide range of hydrogen pressures (6 bar to 200bar), with higher pressure favouring aromatics reduction. Catalysts are generally based on cobalt-molybdenum supported on alumina (so called "cobalt -moly" catalysts Co-Mo/Al<sub>2</sub>O<sub>3</sub>). There are also variants using nickel which are more efficacious in removing nitrogen and possibly oxygen.

#### Pertinent academic literature

Recently Chen *et alia*<sup>3</sup> has shown than lignin derived phenolic compounds including anisole and 1,2-dimethoxybenzene can be hydrogenated to aromatics at atmospheric hydrogen pressure and low temperatures 250-270°C using a molybdenum carbide catalyst. Low selectivity to *cyclo*-hexanes (<10%) was observed.

Shetty *et alia*<sup>4</sup> has also demonstrated the efficacy of molybdenum catalysts for cleaving the C-O bond of hydroxy-aromatics at low hydrogen pressures and low temperatures without leading to saturation of the aromatic ring. In his work cresol was reduced to toluene at 320°C and 1 bar hydrogen.

#### Heavy Oil Hydro-Cracking

Heavy oils (i.e. high boiling point oils, vacuum gas oils, fuel oils) are hydro-cracked at high temperature (typically about 400°C) and high hydrogen partial pressures (>150bar). Catalysts can be either noble metals (platinum, palladium) or transition metals (tungsten, nickel) supported on an acidic catalysts, often a zeolite. The long alkyl chains and large poly-nuclear aromatic molecules are broken up into smaller components for diesel or gasoline blending and non hydrocarbon elements are removed. Because the temperature is lower than in reforming, there is some hydrogenation of aromatics to naphthenes.

Hydro-cracking is known to both decarboxylate and hydrogenate carboxylic acid or esters to produce hydrocarbons.

<sup>&</sup>lt;sup>3</sup> C-J Chen, W-S Lee A Bhan, Applied Catalysis A: General 510 (2016) 42-48

<sup>&</sup>lt;sup>4</sup> M Shetty, K Murugappan, T Prasomsri, W.H. Green and Y Roman-Leshkov, J. Catal., 331 (2015) 86-97

There are many variants on hydro-cracking and one variant has been adapted to process fatty acid methyl esters (such as Collie Coal Product 14) into "green" diesel.

#### **Another Conversion Strategy**

It has been reported by Lindquist and Yang<sup>5</sup> that in the presence of sub-critical water and high temperature and pressure aromatic carboxylic acids (benzoic acid) is degraded to the aromatic at temperatures of 300°C or below.

This should be checked because it would represent a very simple way of upgrading the coal OHD products to aromatic hydrocarbons namely by cutting off the oxygen after production of the primary OHD product and before recovery could lead to *in situ* decarboxylation and the production of saleable BTX minimising the demand for hydrogen.

#### Conclusion

Although coal OHD products are somewhat unique there should exist available technology for removing the oxygen from the products to produce hydrocarbons which would be more readily saleable to the fuels and chemicals industry.

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<sup>&</sup>lt;sup>5</sup> E. Lindquist, Y Yang, *J. Chromat. A* 1218 (2011) 2146-2152

#### POSSIBLE DEVELOPMENT

#### **Features**

Following the above scenario, for the possible development of coal OHD facility, which would hydrogenate the primary oxygenates to aromatics, a process operation would have the following features and assumptions:

Table 5: Principal features of possible coal to aromatics using OHD process

Input	Modelled as Collie coal as received (run of mine)
HHV	18.2GJ/t
Coal production method	Open Cut
Other inputs	None, oxygen and hydrogen produced within the facility.
Hydrogen plant	Coal as feedstock; natural gas is a more efficient feedstock and
	could be substituted if gas is available
Oxygen	On-site air separation unit (ASU)
Utilities	On site, driven by high pressure steam from coal gasifier
	(hydrogen production), hydrogen plant off-gas and fuel gas from
	hydrogenation plant; possible electricity export.
Key unit operations	1. Coal OHD plant; Assumed 100% carbon conversion
	2. Primary product separation from excess water
	3. Primary product hydrogenation
	4. Aromatics plant (commercially available) to separate products
Products	Separate streams of benzene, toluene, mixed xylenes, C9 and C10
	aromatics and naphtha

A simple block flow diagram is shown in Figure 6. Coal from the mine is used for both production of OHD primary products and for the production of hydrogen. The latter is produced by first gasifying the coal into synthesis gas (carbon monoxide and hydrogen). Hydrogen is maximised by water-gas-shift (WGS) and the gas is passed to the hydrogen plant where the hydrogen is separated (membrane or PSA technology). The off-gas is sent to the utilities section along with high pressure steam from the gasifier. The primary role of the utilities is to provide power (or possibly steam) for the air-separation unit which makes oxygen for the gasifier and the OHD plant. Excess power could be exported.

The OHD primary products are separated from the excess water (possibly by solvent extraction) and the water is recycled back to the OHD plant. The primary OHD products are then hydrogenated with any cracked gas or off-gas passed to the utilities section. Note it is assumed that the by-product gases only have fuel value and that co-products such as methanol are not extracted. The mixed aromatic and aliphatic compounds (naphtha) are passed to an aromatics

separation unit (commercially available unit operation) and separated into separate saleable streams.

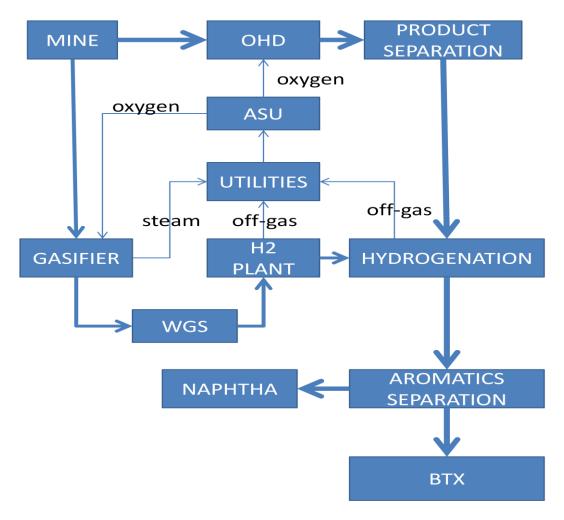


Figure 6: Block-flow diagram for conversion of coal into BTX using OHD route

#### **Outline Economic Statistics**

The outline economic statistics for a greenfield facility are shown in Tables 6 and 7.

Note that for this scenario, more coal is required to produce hydrogen than the OHD primary products (ratio 1.61:1). This is a consequence of the H/C ratio in the coal (0.7) being less than the H/C ratio of the products (1.28) and the need to remove oxygen from the primary products. If natural gas is available it would be more efficient to use gas to produce the hydrogen which would lower capital costs. The operating costs of the facility will also be lower using gas but this will be off-set by the cost of gas imported into the facility.

It is assumed the coal is produced by an open cut operation and the process facility is juxtaposed to the mine site so as to minimise coal carriage cost. It is assumed that the coal could be

produced for \$30/t for run of mine coal and that this quality of coal is adequate for the OHD technology as well as the gasifier without beneficiation.

If 80% of carbon and hydrogen in the coal is converted into BTX and naphtha, this will result in the yields shown in Table. These yields are estimated using the data in column 9 of Table 2. Assuming input coal has a gross calorific value (HHV) of 18.2GJ/t, these yields give a thermal efficiency of 35.5%. This is similar to the efficiency of coal based operations for the production of Fischer-Tropsch fuels from coal in South Africa. This level of efficiency can be improved by converting surplus heat into electricity for export. This has not be considered at this stage.

Toluene, mixed xylene and C9 + C10 aromatics could be sold in Australia for octane blending and displacing imports. Only benzene and naphtha may need to be exported.

Based on crude oil price of \$35/bbl, these statistics give a revenue of \$171/tonne of input coal as shown in Table 7. This results in a cash margin of \$92/tonne of input coal. The process is very sensitive to the prevailing oil price. With oil at \$50/bbl revenue jumps to \$223/t input coal and the gross cash margin to \$145/t of input coal.

Processes of this complexity and type are capital intensive and hence are sensitive to scale of operation. A typical process would require 2.6 million tonnes of coal/year (about 7,500t/d) with 1 million tonnes of coal converted to OHD products. Cash flow from a project of this scale is given in the Summary. Smaller operations could be viable if gas was available to produce the hydrogen.

Table 6: Principal statistics for hypothetical coal to aromatics process using OHD technology

Collie coal input (as received)	tonne	1.000
Percent of carbon and hydrogen present in coal	% (wt)	49.6%
Coal gross calorific value (HHV)	GJ/t	18.2
Hydrogen demand	t/t/t input coal	0.20
Coal for hydrogen production (at 80% efficiency)	t/t input coal	1.61
Yield of hydrocarbons (as % of C and H present in coal)		80%
Benzene	t/t input coal	0.0750
Toluene	t/t input coal	0.1500
Xylenes (mixed including ethylbenzene)	t/t input coal	0.0604
C9 and C10 aromatics	t/t input coal	0.0114
Naphtha	t/t input coal	0.0999
Process thermal efficiency	%	35.5%

Table 7: Principal economic statistics for coal to aromatics technology using OHD technology; prevailing oil price \$35/bbl

Input coal cost		\$/tonne coal	\$30.0
Coal for hydrogen production		\$/tonne input coal	\$48.2
Total coal cost		\$/tonne input coal	\$78.2
Benzene	\$514.6/t	\$/tonne input coal	38.6
Toluene	\$439.1/t	\$/tonne input coal	65.9
Xylenes (including ethylbenzene)	\$477.4/t	\$/tonne input coal	28.8
C9 and C10 aromatics	\$439.1/t	\$/tonne input coal	5.0
Naphtha	\$318.8/t	\$/tonne input coal	31.9
Revenue		\$/tonne input coal	170.95
Cash Margin		\$/tonne input coal	91.95

#### Key assumptions of this possible development which require verification

- 1. The yield of OHD primary products from the coal is very high and that more than 95% of the carbon present in the coal is converted into primary products. This requires a detailed mass and energy balance for Collie coal.
- 2. That the yield is stable with time and repeatable. That the impact of operating conditions on yield is known (oxygen/coal ratio, temperature, pressure).
- 3. The impact of coal quality (batch to batch) on yield and selectivity is known and does not pose a significant operational issue.
- 4. The selectivity to the products is defined over a range of operating conditions and how key operating variables influence primary OHD product selectivity is known. It is assumed in the above econometric analysis that the product distribution as relayed to Duncan Seddon and Associates is typical.
- 5. That a suitable hydrogenation technology based on or similar to a commercially available technology can be identified. That this process produces BTX and naphtha with an overall carbon yield of typically 80% in the proportions as outlined in Tables 1 and 2. Losses are assumed to be fuel gas.

#### Victorian Brown Coal

A similar project could be considered for Victorian brown coal. This would have the advantages of lower coal production costs and the availability of relatively low priced natural gas. However, the economics for VBC are impacted by the larger and more complex product slate which, *prima facie*, would require a higher quantum of hydrogen and would generate a lower yield of BTX relative to naphtha in the final product.

#### POSSIBLE DEVELOPMENT TIME-LINE

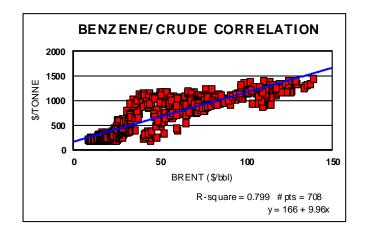
- 1. Construction and operation of a large scale demonstration facility and operation over a six month period to determine yield and selectivity parameters as outline above.
- 2. From the data produce an econometric model for the process
- 3. Approach and discuss unit process operations with significant process licensors and process developers. At a minimum this should include Axens IFP Group Technologies (Paris/Lyon, France) and Honeywell UOP (Des Plaines, Illinois, USA) who are active developers of new technology.
- 4. With input from a process developer, identify hydrogenation route and develop detailed econometric model for the overall process.
- 5. As may be necessary, trial or demonstrate the hydrogenation step
- 6. Produce business plan for development at a suitable level for equity raising or banking finance for a feasibility study. This to include site specifics, detail product sales strategies and discussion with regulatory authorities etc. Raise equity to fund feasibility study and EIS (~\$A4 million).
- 7. Identify suitable design and EPC contractor (Worley Parsons, Lurgi-Krupp etc) with Australian operating experience to conduct bankable feasibility study. Commission EIS.
- 8. Raise capital and banking finance for Front-End Engineering (FEED) and for engineering and construction.
- 9. Commission and start-up.

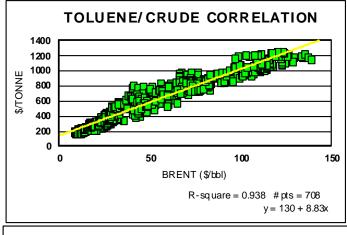
D. Seddon

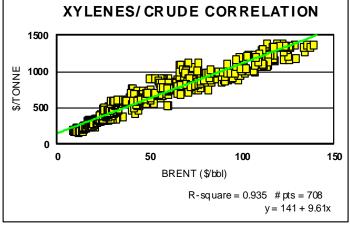
April 2016

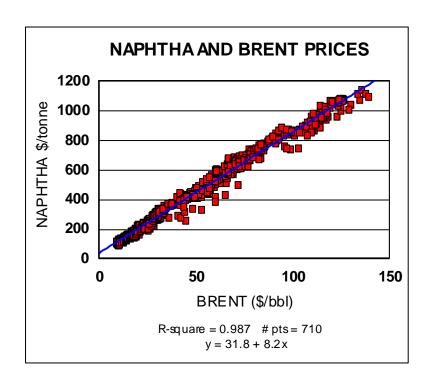
#### **APPENDIX 1**

Correlations of prices of BTX and naphtha (\$/tonne) with Brent crude oil price (\$/bbl, data taken from European Chemical News and ICIS -LORS).







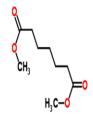


#### **APPENDIX 2**

Some of the compounds of significance produced by OHD of Victorian brown coal (VBC) and Collie coal (CC); diagrams care of *ChemSpider*.

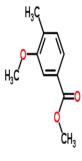
Dimethyl sucinate VBC 3

dimethylpimelate VBC 12

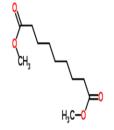


3-methoxy acetophenone VBC 16

Methyl 3-methoxy-4-methylbenzoate VBC 17

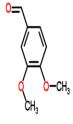


Dimethyl suberate VBC 19



# Dimethylazulate VBC 21

3,4-dimethoxybenzaldehyde VBC 22



Methyl vanillate VBC 23

Methyl 3,4-dimethoxybenzoate VBC 25

2,4-dimethoxyacetophenone VBC 26

Dimethyl sebacate VBC 28

# 3,4,5-trimethoxybenzaldehyde VBC 30

## Dimethyl terephthalate CC4

# CH<sub>3</sub>

# Dimethyl isophthalate CC5

# 6,7-Dimethoxy-m-cymene CC6

# Methyl trimellitate CC16

Dimethyl 2-methoxyterephthalate VBC35, CC15

# Trimethyl trimsate CC17

# 1,7,7-trimethyl 2(1H) Naphthalone CC13