Coal Gasification & Fischer-Tropsch

CCTR Basic Facts File #1

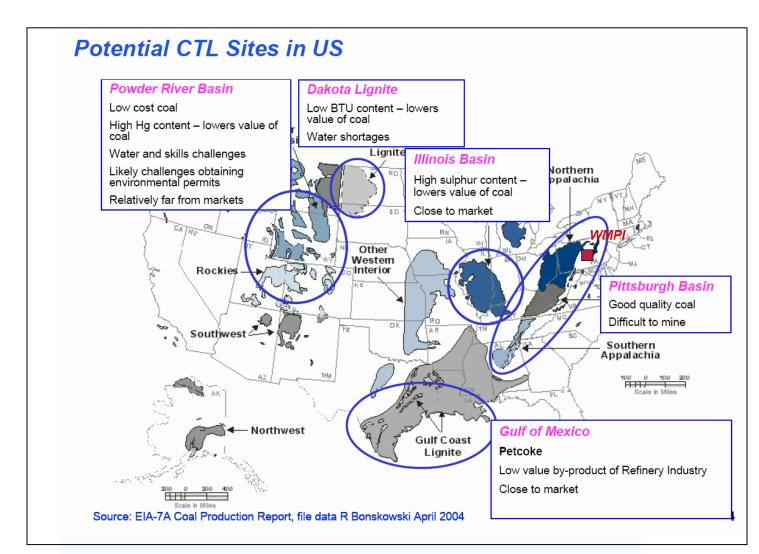
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Fax: 765-496-9322 http://discoverypark.purdue.edu/wps/portal/Energy/CCTR

July 2006

Coal-To-Liquids, CTL

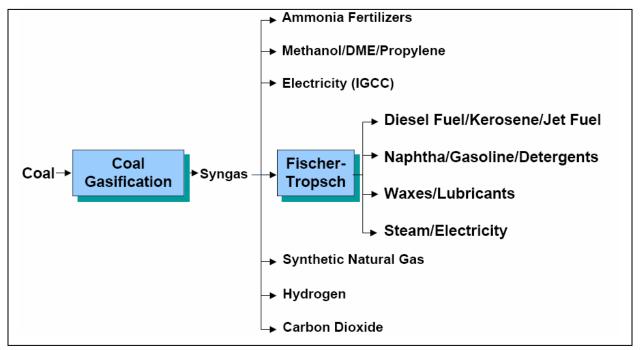




Two main steps in CTL production: (1) First gasify the coal and then (2) Fischer-Tropsch liquefaction process

COAL GASIFICATION FISCHER-TROPSCH

Potential Coal-Derived Products

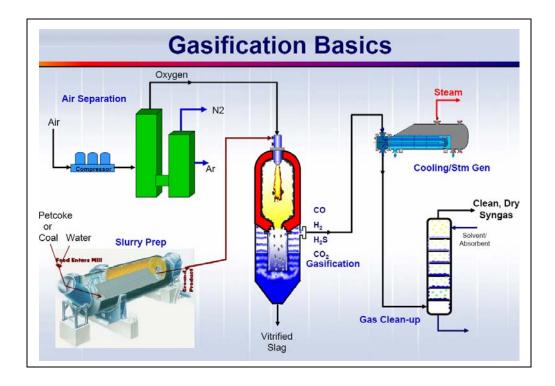


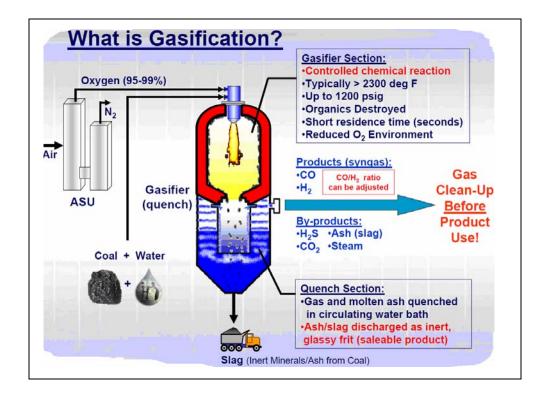
Source: GTI Gasification Symposium, December 2, 2004 <u>http://www.gastechnology.org/webroot/downloads/en/1ResearchCap/1_8GasificationandGasProcessing/L</u> <u>epinskiSmall.pdf</u>

Syngas can be used for power generation (IGCC) or for making fertilizers, methanol, synthetic natural gas, hydrogen or CO_2

Syngas could alternatively be sent through the Fischer-Tropsch process to produce diesel fuels etc

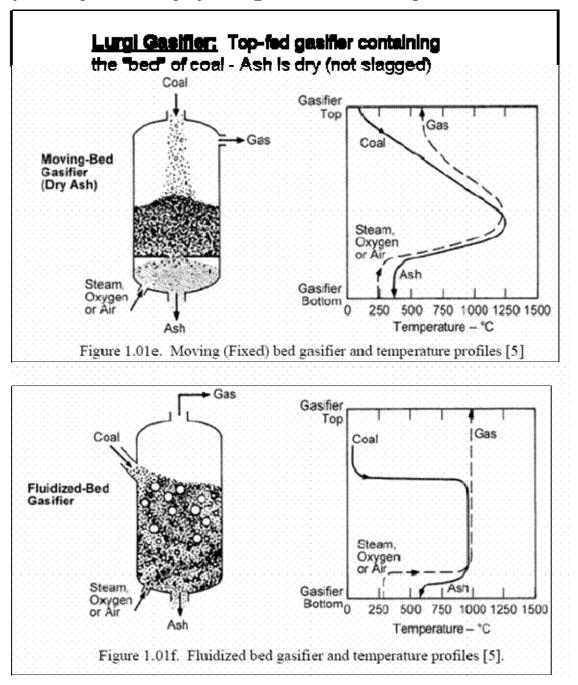
Entrained Flow Gasifier



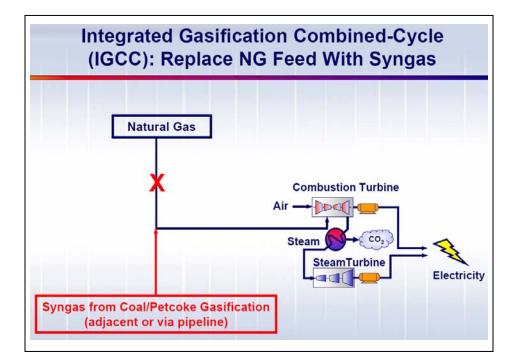


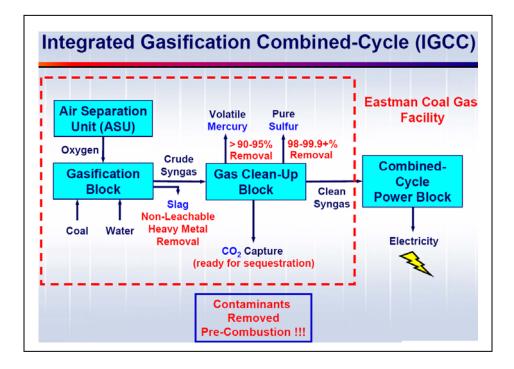
Lurgi Gasifier

BGL - British Gas Lurgi Gasifier has different "bottom" to classical Lurgi - it operates at temperatures above the ash melting point, thus a sing is formed below the "bed" and the ash is discharged as a sing through a quench system – only operating BGL is in Germany.

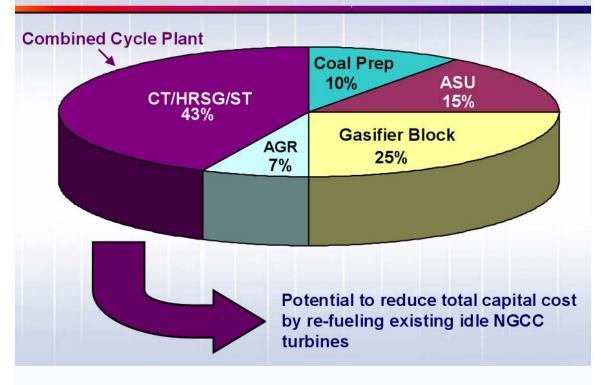


Gasification and IGCC Power Generation









Source: http://www.rrc.state.tx.us/commissioners/williams/energy/Eastman_CO2-1.pdf

Fischer-Tropsch History

Source: http://en.wikipedia.org/wiki/Fischer-Tropsch_process

Since the invention of the original process by the German researchers <u>Franz Fischer</u> and <u>Hans Tropsch</u>, working at the <u>Kaiser Wilhelm Institute</u> in the <u>1920s</u>, many refinements and adjustments have been made, and the term "Fischer-Tropsch" now applies to a wide variety of similar processes (**Fischer-Tropsch synthesis** or **Fischer-Tropsch chemistry**)

The process was invented in <u>petroleum</u>-poor but <u>coal</u>-rich <u>Germany</u> in the 1920s, to produce <u>liquid fuels</u>. It was used by <u>Germany</u> and <u>Japan</u> during <u>World War II</u> to produce alternative fuels. Germany's annual <u>synthetic fuel</u> production reached more than 124,000 barrels per day from 25 plants ~ 6.5 million tons in 1944 (http://www.fe.doe.gov/aboutus/history/syntheticfuels history.html).

After the war, captured German scientists recruited in <u>Operation Paperclip</u> continued to work on synthetic fuels in the <u>United States</u> in a <u>United States Bureau of Mines</u> program initiated by the <u>Synthetic Liquid Fuels Act</u>.

The **Fischer-Tropsch process** is a <u>catalyzed chemical reaction</u> in which <u>carbon</u> <u>monoxide</u> and <u>hydrogen</u> are converted into liquid <u>hydrocarbons</u> of various forms. Typical catalysts used are based on <u>iron</u> and <u>cobalt</u>. The principal purpose of this process is to produce a synthetic <u>petroleum</u> substitute for use as <u>synthetic lubrication oil</u> or as <u>synthetic fuel</u>.

Original process

The original Fischer-Tropsch process is described by the following chemical equation:

$$CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO$$

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2C$$

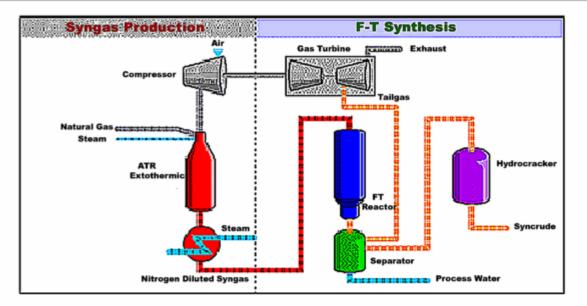
The mixture of <u>carbon monoxide</u> and <u>hydrogen</u> is called <u>synthesis gas</u> or syngas. The resulting hydrocarbon products are refined to produce the desired <u>synthetic fuel</u>. The carbon dioxide and carbon monoxide is generated by partial oxidation of <u>coal</u> and <u>wood</u>-based fuels. The utility of the process is primarily in its role in producing <u>fluid</u> <u>hydrocarbons</u> or hydrogen from a solid feedstock, such as <u>coal</u> or <u>solid carbon</u>-containing wastes of various types. Non-<u>oxidative pyrolysis</u> of the solid material produces syngas which can be used directly as a fuel without being taken through Fischer-Tropsch transformations. If <u>liquid</u> petroleum-like fuel, lubricant, or wax is required, the Fischer-Tropsch process can be applied. Finally, if hydrogen production is to be maximized, the <u>water gas shift reaction</u> can be performed, generating only carbon dioxide and hydrogen and leaving no hydrocarbons in the product stream. Fortunately shifts from liquid to gaseous fuels are relatively easy to make.

Fischer-Tropsch Process

Source: http://www.nationmaster.com/encyclopedia/Fischer Tropsch-process

Action of a catalyst: An increase in the rate of a chemical reaction The Fischer-Tropsch process is a <u>catalyzed</u> <u>chemical reaction</u> in which <u>carbon dioxide</u>, <u>carbon monoxide</u> and <u>methane</u> are converted into liquid <u>hydrocarbons</u> of various forms. Typical catalysts used are based on <u>iron</u> and <u>cobalt</u>. The principal purpose of this process is to produce a synthetic <u>petroleum</u> substitute.

Original process



Fischer-Tropsch Process for Synthetic Diesel Fuel

The original Fischer-Tropsch process is as follows:

$$\begin{array}{l} CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO \\ (2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \end{array}$$

The mixture of <u>carbon monoxide</u> and <u>hydrogen</u> is called <u>synthesis gas</u> or syngas. The resulting hydrocarbon products are refined to produce the desired **synthetic fuel**.

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Liquefaction

Change of a substance from the solid or the gaseous state to the liquid state.

Since the different states of matter correspond to different amounts of <u>energy</u> of the molecules making up the substance, energy in the form of <u>heat</u> must either be supplied to a substance or be removed from the substance in order to change its state. Thus, changing a solid to a liquid or a liquid to a gas requires the addition of heat, while changing a gas to a liquid or a liquid to a solid requires the removal of heat.

In the liquefaction of gases, extreme cooling is not necessary, for if a gas is held in a confined space and is subjected to high pressure, heat is given off as it undergoes <u>compression</u> and it turns eventually to a liquid. Some cooling is, however, necessary; it was discovered by Thomas Andrews in 1869 that each gas has a definite <u>temperature</u>, called its critical temperature, above which it cannot be liquefied, no matter what pressure is exerted upon it. A gas must, therefore, be cooled below its critical temperature before it can be liquefied. When a gas is compressed its molecules are forced closer together and, their vibratory motion being reduced, heat is given off. As compression proceeds, the speed of the molecules and the distances between them continue to decrease, until eventually the substance undergoes change of state and becomes liquid.

Although before the 19th cent. a number of scientists had experimented in liquefying gases, Davy and Faraday are usually credited with being the first to achieve success. The production of liquefied gases in large quantities (and consequently their use in refrigeration) was made possible by the work of Z. F. Wroblewski and K. S. Olszewski, two Polish scientists. The work of Sir James Dewar is also important, especially in the liquefaction of air and its change to a solid. Heike Kamerlingh Onnes first liquefied helium. The critical temperature of helium is -267.9° C, only a few degrees above absolute zero (-273.15° C). The processes for the liquefaction of gases as developed by Linde and others form the basis for those used in modern refrigeration. Liquefied gases are much used in low-temperature research; some, e.g., liquid oxygen, find use as rocket propellants.

Source: http://en.wikipedia.org/wiki/Coal

Among commercially mature technologies, advantage for indirect coal liquefaction over direct coal liquefaction are reported by Williams and Larson (2003). Estimates are reported for sites in China where break-even cost for coal liquefaction may be in the range between 25 to 35 US\$/barrel of oil.

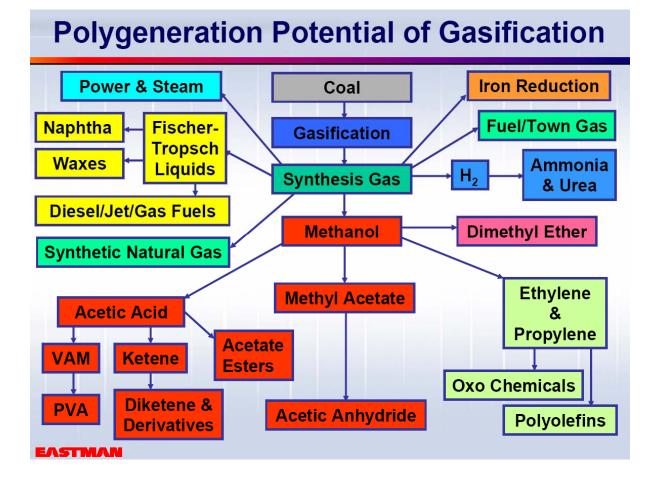
Coal liquefaction is one of the backstop technologies that limit escalation of oil prices. Estimates of the cost of producing liquid fuels from coal suggest that domestic US production of fuel from coal becomes cost-competitive with oil priced at around 35 USD per barrel^[4], (break-even cost), which is well above historical averages - but is now viable due to the spike in oil prices in 2004-2005.^[5].

Coal can also be converted into <u>liquid fuels</u> like <u>gasoline</u> or <u>diesel</u> by several different processes. The <u>Fischer-Tropsch process</u> of indirect synthesis of liquid hydrocarbons was used in <u>Nazi Germany</u>, and for many years by <u>Sasol</u> in <u>South Africa</u> - in both cases, because those regimes were politically isolated and unable to purchase <u>crude oil</u> on the open market. Coal would be gasified to make <u>syngas</u>

(a balanced purified mixture of CO and H_2 gas) and the syngas condensed using Fischer-Tropsch catalysts to make light hydrocarbons which are further processed into <u>gasoline</u> and <u>diesel</u>. Syngas can also be converted to <u>methanol</u>: which can be used as a fuel, fuel additive, or further processed into gasoline via the <u>Mobil</u> M-gas process.

A direct liquefaction process <u>Bergius process</u> (liquefaction by hydrogenation) is also available but has not been used outside <u>Germany</u>, where such processes were operated both during <u>World War I</u> and <u>World War II</u>. SASOL in South Africa has experimented with direct hydrogenation. Several other direct liquefaction processes have been developed, among these being the SRC-I and SRC-II (Solvent Refined Coal) processes developed by <u>Gulf Oil</u> and implemented as pilot plants in the United States in the 1960's and 1970's.^[2]

Products from Coal Gasification & F-T



Review of Fischer-Tropsch Work by Rentech

Table XIV.1				
	No. 1 Diesel ASTM (1)	No. 2 Diesel ASTM (2)	F/T Diesel	
Cetane Index ASTM 976-80	45 min.	40 min.	62	
Sulfur Wt.% ASTM D129-80 90% Distillation	.50 max	.50 max	<0.0001*	
Temperature °F ASTM D56 Viscosity @ 40°C	550°F-max.	540°F-min. 640°F0Max.	556°F	
cSt.	1.4 min.	1.9 min.	1.8	
ASTM D445-82	2.5 max.	4.1 max.		
Conradson Carbon on 10%; ASTM D189-81 Wt.%	.15 max.	.35 max.	.02	
Flash Point ºF, min. Corrected to 760 mm Hg ASTM D56-82	100°F	125⁰F	122ºF	
Aromatic Content, Vol. %; ASTM D1319	8% min.	33%	less than 1%	
API Gravity ASTM D1298	38-41	34.7	48.7	
BTU/lb ASTM D240	16,000-17,000	19,810	19,371	
Oxygen Content, Wt.%	N/A	N/A	3.05%	
 * Analyses were below limits of detection. (1) ASTM D975-81, #1 Diesel (2) ASTM D975-81, #2 Diesel 				

Source: http://crtc.caer.uky.edu/pubs/cobalt/attacXIV.pdf

What a barrel of crude oil makes.

What A Barrel of Crude Oil Makes

Product	Gallons per Barrel
Gasoline	19.4
Distillate Fuel Oil (Includes both home heating oil and diesel fuel)	9.7
Kerosene-Type Jet Fuel	4.3
Coke	2.0
Residual Fuel Oil (Heavy oils used as fuels in industry, marine transportation, and for electric power generation	1.9 N
Liquefied Refinery Gases	1.9
Still Gas	1.8
Asphalt and Road Oil	1.4
Petrochemical Feedstocks	1.1
Lubricants	0.5
Kerosene	0.2
Other	0.4

Figures are based on average yields for U.S. refineries in 2000. One barrel contains 42 gallons of crude oil. The total volume of products made is 2.6 gallons greater than the original 42 gallons of crude oil. This represents "processing gain."

http://www.answers.com/heat%20in%20one%20barrel%20of%20oil

Approximate Heat Content of Petroleum Products

(MBtu per Barrel)

Source: http://www.findarticles.com/p/articles/mi_m2744/is_10_2005/ai_n15863676/pg_2

Monthly Energy Review, October 2005

Petroleum Product

Heat Content

Aviation Gasoline Butane Butane-Propane Mixture (a) Distillate Fuel Oil Ethane Ethane-Propane Mixture (b) Isobutane Jet Fuel, Kerosene Type Jet Fuel, Naphtha Type	5.048 4.326 4.130 5.825 3.082 3.308 3.974 5.670 5.355 5.670
Kerosene Lubricants	6.065
Motor Gasoline	0.005
Conventional (c) Reformulated (c) Oxygenated (c) Fuel Ethanol (d)	5.253 5.150 5.150 3.539
Natural Gasoline and Isopentane	
Pentanes Plus	4.620
Petrochemical Feedstocks	
Naptha Less Than 401[degrees]F Other Oils Equal to or Greater Than 401[degrees]F Still Gas Petroleum Coke Plant Condensate Propane Residual Fuel Oil Road Oil Special Naphthas Still Gas Unfinished Oils Unfractionated Stream Waxes Miscellaneous	5.248 5.825 6.000 6.024 5.418 3.836 6.287 6.636 5.248 6.000 5.825 5.418 5.537 5.796

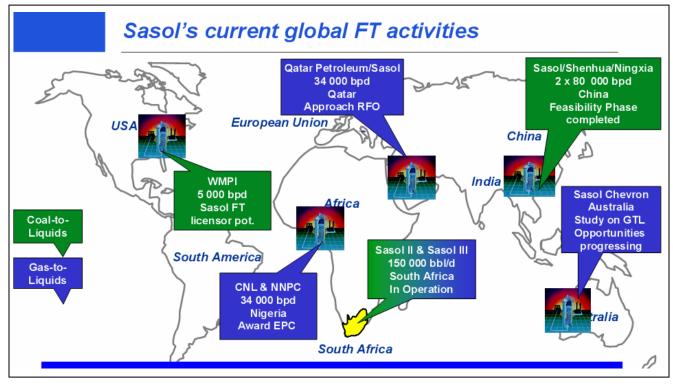
Sasol and Coal-To-Liquids

Sasol Coal-to-Liquids Developments

Presentation to the Gasification Technologies Council Conf, 10-12 October 2005, San Francisco

Eric van de Venter on behalf of Sasol Synfuels International and Sasol Technology (Pty) Ltd Johannesburg, Rep. of South Africa Email: eric vandeventer@sasol.com

Authors: John Sichinga , Nici Jordaan, Maggie Govender, Eric van de Venter



Source: http://www.gasification.org/Docs/2005_Papers/33VAND.pdf

Pennsylvania : WMPI, Coal-To-Liquids SCIENTIFIC AMERICAN MAY 2006

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MAY 2006

Pumping Coal

COMING SOON TO THE U.S.: CLEANER DIESEL FROM DIRTY COAL BY GUNJAN SINHA

ISOLATION TO INNOVATION

Source: http://www.ultracleanfuels.com/pdf/sciam_0506.pdf

Coal-to-liquid technology is not new, but it remains confined to theturf of political pariahs. The technology first emerged in Germany in the 1920s, and the Naz is refined the process to power their warmachine. After the war, the fuel could not compete with the low cost of crude. During the next few decades, however, South Africa took over the reins. Faced with the constant threat of an oil embargo against its apartheid regime, the country tried to wean itself off oil imports. Today the nation's energy giant Sasol holds key patents on certain parts of the process.



FILL 'ER UP: Coal can be converted into diesel fuel and compete with crude oil at about \$60 a barrel.

he U.S. is plump with coal. The country has one quarter of the world's reserves, and coal accounts for about 50 percent of the nation's electricity. To cut the reliance on oil imports, why not also use it to power cars and trucks or to heat homes, too?

That may happen soon. This year Waste Management and Processors, Inc. (WMPI), will break ground for the first U.S. coal-todiesel production facility, in Gilberton, Pa. The plant will process 1.4 million tons of waste coal a year to generate approximately 5,000 barrels a day of diesel fuel. Other states, such as Illinois, Virginia, Kentucky, Wyoming and West Virginia, are also considering coal-to-liquid facilities.

Interest in the technology is certainly welcome news to WMPI president John Rich, who has been trying to finance such a facility

two tons of coal mined, up to half ends ρ in the reject pile," Rich says. Existing nerby facilities are not equipped to burn it. W4PI will rely on approaches innovated by Suth African energy giant Sasol; those metbds are optimized to work with energy-pooroal, which include lignite and bitumen.

The resultant fuel is cleaner than coventional, sulfur-free diesel. In comparison sts, DaimlerChrysler showed that the coaderived fuel spews 10 percent of the car bon monoxide and hydrocarbons and 70 percent of the particulates. The firm had plans to unveil a demonstration vehicle with a tweaked V-6 engine in April that cuts nitrogen oxides and other emissions even further, says Stefan Keppeler, senior manager of fuels research at the company.

Though relatively clean at the tailpipe, the fuel is dirty at its source. A similar coal-based power plant discharges about four million tons of carbon dioxide a year. In some facilities, the greenhouse gas can be repurposed-it can be pumped into oil fields or, in the case of WMPI's plant, sold to the beverage industry. Unless scientists develop methods to sequester CO2 and find other uses for the gas, the technology might languish, warns Rudi Heydenrich, business unit manager at Sasol. The gasification step is also expensive, accounting for two thirds of the cost of a facility. "You need a structure

for more than a decade. "Coal to liquids hadn't taken off, because the price of crude was at \$30 to \$40 a barrel," Rich says. Oil at about \$60 makes coal more attractive.

To create the fuel, coal is first mixed with oxygen and steam at high temperature and pressure to produce carbon monoxide and hydrogen. The second step, referred to as Fischer-Tropsch synthesis, uses a catalyst to transform the gas into a liquid synthetic crude, which is further refined. Along the way, mercury, sulfur, ammonia and other compounds are extracted for sale on the commodities market.

The type of technology required to gasify the coal depends on the starting material. Pennsylvania alone has an estimated 260 million tons of waste coal—coal discarded because of its low energy content. "For every

where there is government support to ensure sustainable economics in the long run," Heydenrich remarks.

Under the Bush administration's

Clean Coal Power Initiative, a \$100-million federal loan guarantee jump-started the new WMPI facility. The state of Pennsylvania also chipped in with tax credits and a plan to buy up to half the plant's output to power its vehicles. Investors may contribute the additional \$500 million necessary to build the plant. The initial cost of the fuel is expected to be about \$54 a barrel.

Coal is not the only source of synthetic

diesel; the fuel can be derived from natural gas and more cheaply, too. In fact, Qatar and Nigeria are building gas-to-liquid plants, and Sasol estimates that by 2014, gas-to-liquid fuel may account for at least 5 percent of the global market. But the U.S. does not have nearly as much natural gas as coal. And considering the vast coal reserves in China, which is also considering the technology, coal-derived diesel seems likely to play a bigger role in helping to liberate some countries from dependence on oil imports.

Gunjan Sinha is based in Berlin.

Arizona, N. Dakota: Headwaters and Coal-To-Liquids

NEWS BULLETIN

FROM:

F I N A N C I A L RELATIONS BOARD

AT THE COMPANY:

FOR FURTHER INFORMATION

Sharon Madden Director of Investor Relations (801)984-9400

FOR IMMEDIATE RELEASE: August 9, 2005 RE: Headwaters Incorporated

10653 South River Front Parkway, Suite 300 South Jordan, UT 84095 (801) 984-9400 NYSE: HW

AT FINANCIAL RELATIONS BOARD: Tricia Ross Analyst Contact (617) 520-7064

HEADWATERS INCORPORATED ANNOUNCES COAL-TO-LIQUIDS AGREEMENTS

SOUTH JORDAN, UTAH, August 9, 2005 (NYSE: HW) – HEADWATERS INCORPORATED announced today that it has completed two non-binding Memoranda of Understanding ("MOUs") linked to potential coal-to-liquid fuels projects in Arizona and North

Dakota. Parties to the Arizona project include Headwaters and the Hopi Tribe. Parties to the North

Parties to the Arizona project include Headwaters and the Hopi Tribe. Parties to the North Dakota project include Headwaters, Great River Energy, North American Coal Corporation and Falkirk Mining Company.

Each MOU anticipates Headwaters will act as the principal developer of an indirect coal liquefaction plant that will produce approximately 10,000 barrels per day of ultra clean diesel and other liquid fuels, as well as electricity from an IGCC power station. Plant expansions could increase output up to 50,000 barrels per day of liquid fuel production. The other parties to the MOUs will participate as equity partners in the project development and will contribute coal resources sufficient to serve the lives of the respective plants.

Development of each project will be subject to negotiation of definitive agreements, permitting, Board of Directors' approvals, project financing and other conditions. Headwaters estimates that design and construction of a facility, including the permitting, will take between five and seven years. Although the projects are major undertakings in their preliminary stages, Headwaters believes that the demand for liquid fuels today and over the next 20 years will drive the continued development of America's coal assets.

Illinois: Coal Gasification for Methane (GTI Chicago)

April 26, 2006

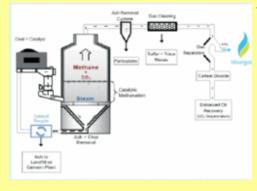
GreatPoint Energy Catalytic Coal Methanation



GreatPoint Energy is developing a gasification process for converting coal into high value clean natural gas which they call Bluegas[™]. The gas is 98% methane (1000 BTU/ft³), meeting all natural gas purity requirements and can be transported using the existing natural gas pipeline infrastructure. The company plans on building, owning and operating the production facilities and to sell the gas. Because domestic natural gas has passed peak production rates, the US has the world's largest coal reserves and because natural

gas is the fuel of choice for many uses; given a low cost source of gas, the company believes there is a huge potential market for their gas.

GreatPoint Energy's technology uses the same basic technique as is used in petroleum refining to "refine" coal by employing a novel catalyst to "crack" the carbon bonds and transform the coal into clean burning methane (natural gas). This single stage process is called catalytic coal methanation and forms the basis of their process. By adding a catalyst to the coal gasification system, they are able to reduce the operating temperature in the gasifier and at the same time directly promote the reactions that yield methane (CH4). Very low cost carbon sources (such as lignites, sub-bituminous coals, tar sands, petroleum coke and petroleum resid) can be used as feedstocks.



The process produces methane in a single step and in a single reactor. In the process, (shown at left, click to enlarge) coal and catalyst are fed to a fuidized bed methanation reactor. Steam is added to "fluidize" the mixture and ensure constant contact between the catalyst and the carbon particles, generating a gas of predominately methane and

CO₂. The water gas shift occurs within the methanation reactor eliminating the need for a separate reactor.