CHARACTERIZATION OF THE PRODUCTS OF MILD GASIFICATION AT THE UNIVERSITY OF NORTH DAKOTA ENERGY AND ENVIRONMENTAL RESEARCH CENTER

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ABSTRACT

The primary objective of the Energy and Environmental Research Center (EERC) Mild Gasification project has been to demonstrate a process that will produce several value-added products from a high-sulfur midwestern bituminous or a low-sulfur western subbituminous coal. Indiana No. 3 and Wyodak were the coals used for the majority of testing. The products of the process are a low-Btu gas, a hydrocarbon condensate, and a low-volatile char.

The testing was carried out on 4- and 100-lb/hr units. Initial yield data were generated using the 4-lb/hr continuous fluid-bed reactor (CFBR). The preliminary data were then used to plan production runs on the 100-lb/hr process research unit (PRU). An extensive survey was conducted to determine possible markets for the products. The survey indicated that the best slate of products would consist of a metallurgical form coke product from the solids, a feedstock for specialty chemicals from the liquids, and the gas being burned in the plant for utility heat or in a small electric cogeneration unit. The program was then tailored in an attempt to optimize the raw products to meet the industry standards for the desired end products. In the area of form coke, the EERC investigated organic and inorganic binders in both pelletizing and briquetting schemes. The heavy pitch fraction of the liquid products can be utilized as an organic binder in the briquetting process. The lighter liquids have been analyzed to determine their potential as a source of cresylic acid as well as for use as a liquid motor fuel.

INTRODUCTION

Coal is the largest indigenous energy resource in the United States. As the price of oil, both foreign and domestic, increases, it will become necessary to tap America's vast coal reserves to augment and in some cases to replace the use of petroleum. The replacement of oil with coal in production of electric power is relatively simple, and the EERC also proposes the use of coal in the chemical market.

The mild gasification process is similar in concept to an oil refinery in which a varied slate of products can be produced from a raw feedstock. The capability to alter product distributions, either by changing feedstocks or process conditions, would permit timely response to the ever-changing market. The current mild gas process consists of a rapid devolatilization of raw coal under mild conditions of temperature and pressure, resulting in a low-Btu gas, a hydrocarbon condensate, and a reactive, low-volatile char.

RESULTS

The major findings of the work at the EERC in mild gasification are summarized based on data from the tests on Indiana No. 3, Wyodak, and Cannelton coals in the thermogravimetric analyzer (TGA), the CFBR, and the PRU. All yields reported are as percentages of moisture- and ash-free coal.

The Effect of Process Conditions on Char Yield and Char Quality for Indiana No. 3, Wyodak, and Cannelton Coals

PRU Test Results

Operability of the PRU carbonizer was satisfactory for both the Indiana No. 3 and Wyodak coals. Table 1 shows the char yields and char quality from tests on the PRU and CFBR. The Indiana char values are for cleaned and uncleaned char. The lower yields for the cleaned char are due to the amount of char that is rejected in each gravity/magnetic separation that occurs between processing steps. No internal oxidation was assumed, which raised the carbonizer yield by 16%. Internal oxidation was only used to maintain reactor temperature due to heat loss.

The Wyodak char was the only char that met metallurgical coke specifications. The volatile content was higher than typical coke; however, testing indicated that briquettes produced from this char had acceptable strength properties. The Cannelton char data are reported without physical cleaning. If the relative reduction of ash in the Indiana No. 3 char can be used as a comparison, the Cannelton char could be reduced to 12%-13% ash, which would be slightly higher than the specifications. The volatile content is quite low, which should produce a high-strength coke substitute. The Indiana char did not meet the ash or sulfur content desired.

Char yields in the PRU with internal oxidation for the Indiana tests varied from 44.9% to 59.3% over a temperature range of 1020° to 1200°F (550° to 650°C) with limited agglomeration that presented no operational difficulties. The major variation was due to oxidation in the reactor for some test points in order to meet the desired run temperature. Only one mass balance was completed for the Wyodak coal, which had a yield of 49% at 1100°F (600°C).

CFBR Test Results

Operability of the CFBR was satisfactory on noncaking Wyodak subbituminous coal. Satisfactory operation on mildly caking Indiana No. 3 and Cannelton bituminous coal was accomplished only by temperature staging, using char produced at lower-temperature runs as feed for a subsequent run at a higher temperature. Temperature stages used were 660°, 750°, 840°, 930°, and 1470°F (350°, 400°, 450°, 500°, and 800°C). Other methods that were tried for controlling agglomeration were of very limited success, including preoxidation of the coal feed, internal oxidation, and use of a limestone bed.

Char yields were determined in the CFBR between 930° and 1110°F (500° and 600°C) for Wyodak coal, at staged temperatures between 660° and 1470°F (350° and 800°C) for Indiana No. 3 coal, and at staged temperatures between 660° and 1290°F (350° and 700°C) for the Cannelton coal. The char yields decreased with increasing temperature and were significantly higher for the Indiana No. 3 coal, which yielded about 74 wt% char at 930°F (500°C) and 61 wt% at 1470°F (800°C). Corresponding yields for Wyodak were about 60 wt% at 930°F (500°C) and 50 wt% at 1110°F (600°C). Yields for the Cannelton coal were 82 and 74 wt% at 930° and 1290°F (500° and 700°C), respectively.

A calcining temperature of 1470°F (800°C) was needed to reduce the volatile content of the Indiana No. 3 char below 10%, as required for use in form coke. At this temperature, a typical analysis for Indiana No. 3 char was 8.5% volatile matter, 74% fixed carbon, 19% ash, and 3.4% sulfur without upgrading.

The Effect of Process Conditions on Condensable and Gas Yields

PRU Test Results

A wide variety of yields and boiling point distributions were observed for the three coals, as shown in Table 2. This table has data from the PRU and the CFBR. The Wyodak condensables approximated a liquid that was lighter than a decant oil (#6 diesel). The Indiana No. 3 liquids were the lightest and produced a 17.8% yield. Gas yields are shown in Table 3. The Indiana No. 3 yields are adjusted for no internal oxidation, which resulted in a reduction of CO_2.

Initially, operation difficulties were encountered with the tar scrubber. The problems were eliminated by lowering the outlet temperature of the tar scrubber and redesigning the scrubber cyclones to eliminate mist entrainment. This increased the amount of liquid condensed in the scrubber, decreasing the coal fines/liquid ratio. The lower outlet temperature increased the light oil content of the recycle loop. This light oil then acted as a solvent for the heavy tars.

The sieve tower and water scrubber performed very well over a wide range of gas velocities and heat loads. During the course of operation, the outlet temperature of the sieve tower was reduced to below the dew point of water, in response to the reduction in outlet temperature of the tar scrubber. This reduced the heat duty on the water scrubber that served as a backup unit to remove entrained organics from the sieve tower.

CFBR Test Results

Total gas yield for the Wyodak coal ranged from 31% to 51% between 930° and 1110°F (500° and 600°C), generally increasing with temperature. The total yield of gas from Indiana No. 3 coal ranged from a low of 2% to 5% at 660°F (350°C) to about 20% at 1470°F (800°C). Yields of all major gas components generally increased along with temperature. The measured gas compositions varied widely, but typical ranges were 50% to 70% for CO_2, 8% to 14% for CH_4, 3% to 12% for CO, and up to 3% for H_2.

Yields of condensable organic liquids were higher for Indiana No. 3 bituminous coal than for Wyodak subbituminous. The cumulative yields obtained by staged heating of Indiana No. 3 coal increased along with temperature from less than 1% at 660°F (350°C) to about 18% at 930°F (500°C) and remained at 18% at the calcining temperature of 1470°F (800°C), owing to essentially zero liquid yield upon further heating of product char prepared at 930° to 1470°F (500° to 800°C). The maximum yield was less than that predicted by the Fischer Assay correlation, possibly due to the short residence time of the fine coal/char feed fraction in the fast fluidized-bed reactor.

The liquid yield for Wyodak coal was highest (10.7%) at the lowest test temperature of 930°F (500°C), and decreased by varying amounts to levels between 0.2% and 9.7%, depending on the gas atmosphere in the carbonizer.

The gas yield for the Cannelton coal was considerably lower than for the other two coals. Yields varied from 5% to 8% at temperatures from 930° to 1290°F (500° to 700°C). Condensable yields ranged from 14% to 19% over the same temperature range, with a large quantity in the 430° to 700°F (220° to 370°C) boiling point range. The most important feature of the Cannelton liquids was the quality. It resembled a #3 diesel fuel.

The Effect of Gas Atmosphere Including Steam on Liquid Yield and Quality (CFBR Test Results)

The use of steam increased the liquid yield from Wyodak coal in three different gas atmospheres, including 1) CO_2; 2) N_2/CO_2, representing flue gas; and 3) $N_2/CO_2/2\%\ O_2$, representing flue gas with excess air. The effect of steam was noted primarily at the highest test temperature of 1110°F (600°C), where in all cases an increase in steam partial pressure caused an increase in liquid yield, which, in the case of the N_2/CO_2 gas atmosphere, amounted to an increase from 0.2% liquid at 21% steam to 9.7% at 88% steam. The presence of 2% O_2, surprisingly, did not reduce the liquid yield, which was higher with 2% O_2 than for N_2/CO_2 alone at a low-steam partial pressure and which was about the same at higher levels of steam. At the lower temperatures of 1020° and 930°F (550° and 500°C), the Wyodak liquid yield varied with steam partial pressure in a manner that did not define a systematic trend.

For Indiana No. 3 coal, liquid yield increased consistently, but only slightly, along with an increase in steam at lower staging temperatures between 660° and 750°F (350° and 400°C). At higher temperatures, no consistent trend was observed.

The boiling point profiles and compound distributions for the two test coals differed, as shown in Table 4. The 3% to 4% low boiling aromatic fraction (BTX) is believed to be lower than the amount actually produced because of losses in the condensation train. Wyodak coal when carbonized without steam produced the highest yield of phenolics, boiling between 330° and 430°F (170° and 220°C). The 430° to 700°F (220° to 370°C) fraction was higher for Indiana No. 3 coal, but the even higher boiling pitch fraction was nearly missing for this coal as tested.

The most prominent effect of steam was to promote higher liquid yields from Wyodak coal at the higher carbonization temperature of 1110°F (600°C). At this condition, the steam is believed to have prevented the retrograde condensation and polymerization of organic compounds on the highly reactive surface of the Wyodak char. Another possible scenario is that the steam provides a better mechanism for removing the tar from the char pore structures. At any given temperature, the condensable yield with steam produced an amount of liquids equivalent to that produced under a higher operating temperature without steam.

The Effect of Process Conditions on Sulfur Removal

Sulfur reduction played a major role in the development of the process, as the main feed coal had a sulfur content over 4.2%. Since the program was to provide engineering data for commercialization, only proven, low-cost sulfur-reduction techniques were reviewed and incorporated into the process.

A series of tests were conducted to establish the database using a TGA and the CFBR in conjunction with analytical techniques that include scattered electron microscopy (SEM) with elemental mapping. A summary of the findings on in-process sulfur removal includes the following points:

- Pyritic sulfur was effectively reduced to low levels, but organic sulfur, as defined by ASTM analytical methods, was not appreciably reduced.

- Residence time had an important influence on the amount of pyritic and total sulfur removed. The effect extended beyond the 20- to 30-minute residence time at staging temperatures in the TGA and CFBR, since the greatest reduction in total sulfur content (from 3.9% to 1.2%) was observed after 6 hours of residence time in the 30-lb/hr fluidized-bed reactor.

- Gas atmosphere had a minor effect on sulfur removal. Larger reductions in total sulfur content in TGA tests were noted in either reducing (CO or H_2/CO) or oxidizing atmospheres than in N_2. The use of steam in the 4-lb/hr CFBR did not increase the extent of sulfur removal.

- The chemical forms of sulfur in char were found to be more complex than the pyritic, sulfitic, and organic forms defined by the ASTM procedure. Analysis of char surfaces using scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and electron spectroscopy for chemical analysis (ESCA) indicated that important changes in the physical and chemical form of sulfur occurred at 720° to 840°F (380° to 450°C) coincident with the onset of coal agglomeration and with the loss of sulfur from pyrite (FeS_2 to FeS). The principal change observed was that discrete crystals containing sulfur (possibly pyrite) present at 660°F (350°C) had disappeared at 840°F (450°C) and were replaced by a low concentration of sulfur that was detected over the entire char surface. SEM mappings of elements indicated some coincidence in the location of sulfur with Fe and Ca.

- After heating to calcining temperatures, most of the sulfur remaining in the coal is in the ASTM organic form. No combination of time, temperature, and gas atmosphere investigated in this study was successful in systematically removing this stable form of "organic sulfur."

Results of Char Upgrading for the Production of Metallurgical Coke Substitutes Using Inorganic Binders (PTC Process)

Table 5 includes a compilation of the compressive strengths, impact numbers, and tumble tests for the green pellets, dried pellets, and hardened pellets for the char with/without limestone. The individual tests for inorganic and organic binders use slightly different methods, so only general comparisons can be made between the two binders.

The initial Wyodak char submitted to Pellet Technology Corporation (PTC) for testing contained an uncharacteristically high ash content of 27%, owing to contamination from the limestone bed in the 30-lb/hr fluidized-bed reactor used to produce this bulk sample.

- CaO-SiO_2-bonded carbon pellets and carbon-iron ore pellets of 1-inch diameter were successfully produced by induration in saturated steam at 420°F (215°C) and 300 psig.

- The finished pellets exhibited satisfactory strength, density, and abrasion resistance with 10% CaO-SiO_2 binder, but not with 5% binder. Since the addition of inorganic binder increases the amount of slag in the iron smelting process, a smaller amount of binder would be a significant benefit.

- The char-iron ore pellets were reduced to iron metal at very high rates upon heating to 2700°F (1480°C). The 5 minutes required for reduction was estimated to be fivefold less than it would have been using coke-iron ore pellets, owing to the high reactivity of the Wyodak char.

The inorganic tests yielded marginally acceptable compressive strength pellets for the Indiana No. 3 and Wyodak chars. The char-iron ore agglomerates were superior in all categories. The sulfur and volatile contents of the agglomerates are considerably lower since they are made of 25% char and 75% iron ore.

Results of Char Upgrading for the Production of Metallurgical Coke Substitutes Using Organic Binders

The Wyodak and Indiana chars were briquetted using a variety of organic binder types and binder levels that ranged from molasses and starch acrylic copolymer emulsions to coal-derived liquids. The briquettes were then subjected to compressive strength, tumble, and impact tests for the purpose of comparison with PTC pellets. The following is a summary of the organic binder briquette tests:

- Indiana and Wyodak chars when mixed with the asphalt emulsions, FMC formcoke® pitch, P028 scrubber tar, and P027 scrubber tar distillation resid as binders yielded durable oven-cured tablets with high compressive strengths.

- When the briquettes of Indiana char together with 15 wt% P027 scrubber tar distillation resid and the briquettes of Wyodak char with 20 wt% P028 scrubber tar were coked, their strength approached that of FMC formcoke®.

- Wyodak or Indiana char briquettes containing 15 wt% or less P028 scrubber tar or 15 wt% asphalt emulsion did not meet the strength criteria.

- Coked Indiana and Wyodak char briquettes were resistant to moisture absorption under simulated conditions of water soaking and rain showers.

- Wyodak char briquettes, with strength and durability similar or superior to that of a commercial barbecue briquette, can be prepared using starch binders at concentrations of ~4 wt%. Exceedingly strong briquettes with almost complete shatter and abrasion resistance can be prepared with 7 wt% starch.

Table 5 includes a compilation of the compressive strengths, impact numbers, and tumble tests for the dried pellets and hardened pellets for the two chars. The two examples shown in the table are those with the coal-derived liquid. The Wyodak pellet had a high sulfur content due to the use of Indiana tar as the binder, and the char produced was a combination of Wyodak and Indiana No. 3 char.

Results of Char Upgrading for the Production of Activated Carbon

The production of activated carbon for use in the adsorption of SO_2 was investigated by producing calcined char with a small amount of steam present in the reactor. The resulting char was pelletized using the PTC process to provide a uniform particle of sufficient size and strength to be used in a filter device.

Sulfur capture was determined by using a TGA with an argon/sulfur dioxide sweep gas. The activated carbon produced at 1380°F (750°C) with 26% of the fluidization gas being steam had the highest SO_2 adsorption. The char increased in weight by 8.1%. Pelletizing the char had no effect on the adsorption capabilities of the char and produced a product that had much better material-handling capabilities. Higher steam partial pressures should be investigated as the experimental matrix did not find the upper limit of steam partial pressure in relation to increased SO_2 adsorption.

Results of Condensable Upgrading for the Production of Cresylic Acid

The Indiana No. 3 liquids yielded cresylic acids in quantities less than 5% of the original sample. It would not be economical to recover such a small quantity of cresylic acid from the liquid stream. However, the Wyodak condensables that were provided to Merichem from the Western Research Institute (WRI) mild gasification project contained 40% usable cresylic acids. This amount merits further consideration into the economic merits.

Results of Condensable Upgrading for the Production of Diesel Fuel Additives

The results from the diesel fuel testing being conducted by Oak Ridge National Laboratories under a separate DOE contract were not available by the publication deadline.

TABLE 1. Char Yields and Quality

	Coal Specifications	Wyodak[a]	Indiana[b]	Indiana[c]	Cannelton
930°F		60.0	74.0		81.7
1110°F		49.0	68.0	54.4	
1290°F			55.1	30.1	74.3
Proximate Analysis, wt%					
Temperature, °F		1110	1290	1290	1290
Fixed Carbon		74.6	65.3	59.6	73.1
Volatiles	<10	15.0	10.3	10.3	6.7
Moisture		1.5	2.0	0.6	0.5
Ash	<10	8.9	22.5	16.1	19.7
Sulfur	<1	0.5	3.5	2.9	0.8

[a] Uncleaned.
[b] No internal oxidation.
[c] Cleaned (low yields due to coal reject in cleaning steps).

TABLE 2. Condensable Yields and Quality

	#2 Diesel	Decant Oil	Wyodak		Indiana		Cannelton		
	%	%	Yield	%	Yield	%	Yield	%	
ibp - 330°F	10		0.3	3	0.7	4	0.1	1	Gasoline Octane Enhancers, Benzene
330° - 430°F	86		3.2	34	6.2	35	2.7	14	Cresylic Acids, Phenols
430° - 700°F	4	44	3.9	41	10.7	60	14.1	74	Diesel Fuel Blends
700° - 1020°F		56	2.1	22	0.2	1	2.1	11	Briquetting Binders, Anode Carbon
	100	100	9.5	100	17.8	100	19.0	100	

TABLE 3. Gas Yields

	Wyodak	Indiana[a]	Cannelton
930°F	31.0	10.0	5.0
1110°F	42.0	19.0	
1290°F		22.0	8.0

[a] No internal oxidation.

TABLE 4. Comparison of Wyodak and Indiana No. 3 Condensable Boiling Point Fractions

	Percent of Liquid Produced		
Boiling Point Range and Major Compound Type	Wyodak 1110°F 0% Steam	Wyodak 1110°F 99% Steam	Indiana Staged to 1470°F 30% Steam
ibp to 330°F, BTX	4.0	3.4	3.6
330° to 430°F, phenolics	44.0	34.1	35.4
430° to 700°F, multiring aromatics and alkylated phenolics	34.7	40.6	59.6
above 770°F, crude pitch	17.4	21.9	1.4

TABLE 5. Summary of Inorganic and Organic Pelletizing Tests[a]

	Indiana No. 3 PTC Process Inorganic Binder	Indiana No. 3[b] PTC Process Inorganic Binder	Wyodak PTC Process Inorganic Binder	Wyodak[b] PTC Process Inorganic Binder	Wyodak[c] PTC Process Inorganic Binder	Indiana No. 3 Organic Binder[d]	Wyodak Organic Binder[e]
Inorganic Content	24.4	76.2	26.0	77.9	47.8	27.0	21.0
Sulfur Content	3.3	0.6	0.8	0.2	0.6	2.8	3.0
Volatile Content	10.6	2.1	10.2	2.1	7.7	<6.0	5.4
Green Pellets							
Compressive Strength, lb	13.6	7.7	16.7	9.9	30.6		
Impact Number	>26.0	6.4	>25.0	12.3	45.6		
Dried Pellets							
Compressive Strength, lb	6.4	5.4	7.7	7.0	1.5	108.0	89.0
Impact Number	2.0	1.0	2.0	1.6	1.5		
Hardened Pellets							
Compressive Strength, lb	20.3	146.4	46.2	104.0	340.0	163.0	54.0
Impact Number	5.2	>25.0	16.8	>25.0	>100		
Density, g/cm^3	1.3	2.5	1.0	2.4	2.1	1.1	1.0
Tumble Test, %							
+3 mesh	68.0	98.0	92.5	97.2	98.2	69.0	87.0
+14 mesh	2.8	0.2	0.2	0.1	0		
-14 mesh	29.2	1.8	7.4	2.7	1.8		

[a] Numbers reported are those for the coke produced that provided the best specifications. The PTC pellets reported here are only char.
[b] Iron/char agglomerate.
[c] Wyodak char contained 15% limestone.
[d] Crushed Indiana char with 15% coal-derived tar and 15% limestone.
[e] Crushed Wyodak char with 4.1% Sta-Lok and 4.5% Indiana coal-derived tar.