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**Energy and Environmental Research Emphasizing
Low-Rank Coal -- Task 3.9
Catalytic Tar Cracking**

Topical Report

Ronald C. Timpe

Work Performed Under Contract No.: DE-FC21-93MC30097

For
U.S. Department of Energy
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September 1995

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TASK 3.9 – CATALYTIC TAR CRACKING

1.0 INTRODUCTION

Tar produced in the gasification of coal is deleterious to the operation of downstream equipment, including fuel cells, gas turbines, hot-gas stream cleanup filters, and pressure-swing absorption systems. Catalytic cracking of tars to smaller hydrocarbons can be an effective means of removing these tars from gas streams and, in the process, generating useful products, such as methane gas, which is crucial to operation of molten carbonate fuel cells.

The need for on-line cracking of gasification tars is common to many types of gas stream cleanup. Aerosol tars are not readily removed from gas streams by conventional means and, as a consequence, often end up plugging filters or fouling fuel cells, turbines, or sorbents. Catalytic cracking of these tars to molecular moieties of C_{10} or smaller would prevent the problems commonly attributed to the tars. As an example, the moving Bourdon (fixed-bed) gasifier, by virtue of its efficient countercurrent heat exchange and widespread commercial use, may offer the lowest-cost integrated gasification combined-cycle (IGCC) system if tar generation and wastewater contamination can be minimized. A project has been undertaken on catalytic tar cracking to evaluate the potential of selected catalysts to minimize tar accumulation and maximize char conversion to useful liquid and/or gaseous products.

2.0 SPECIFIC OBJECTIVES

The objectives of this project arise from two fundamental questions concerning catalytic cracking of tar:

1. Can gasification tar be cracked by synthetic nickel-substituted mica montmorillonite (NiSMM), zeolite, or dolomite material to a product slate that does not contaminate downstream equipment such as ceramic or candle filters, fuel cells, or turbines?
2. Can gasification tars be cracked selectively by the catalysts mentioned above to produce a desired liquid and/or gas stream?

3.0 EXPERIMENTAL

3.1 Materials

Three low-rank coals (LRCs)—a leonardite, a lignite, and a subbituminous coal—were chosen for testing the tar-cracking capability of NiSMM, dolomite, and zeolite. North Dakota leonardite was selected as a LRC to be pyrolyzed to test the effect of NiSMM in cracking pyrolysis tar. The proximate analysis of the leonardite is shown in Table 1. Previous experience with NiSMM as an in-bed gasification catalyst for the steam-leonardite reaction indicates that it does not effectively increase the rate of gasification but seems to promote the production of more methane than obtained from uncatalyzed gasification. The leonardite, however, is not an abundant

TABLE 1

Proximate Analysis of Leonardite and Lignite Gasification Feedstock

Coal	Moisture, AR ¹ , wt%	Volatiles, mf ² , wt%	Fixed Carbon, mf, wt%	Ash, mf, wt%
Leonardite (ND)	42.1	49.9	37.6	12.2
Beulah – West Pit (ND)	30.2	44.8	47.6	7.6
Beluga (AL)	17.6	46.5	46.0	7.6

¹ As-received.² Moisture-free.

fuel and therefore not a serious candidate for the remainder of the study. The large reserves of lignite are excellent candidates for gasification, as demonstrated by the Dakota Gasification Company at Beulah, North Dakota, which gasifies more than 15,000 tons of lignite per day. After the initial NiSMM tests with leonardite, Beulah West Pit lignite was the substrate gasified to provide the tar. The proximate analysis of Beulah West Pit lignite is shown in Table 1.

Following the test series with lignite, three tests at 800°C were carried out with Beluga Alaskan subbituminous coal. One test was carried out without a tar-cracking catalyst, one with dolomite, and one with zeolite as a tar-cracking catalyst. The proximate analysis of the subbituminous coal is also shown in Table 1.

3.2 Method

Pyrolysis and steam gasification were carried out in the integrated bench-scale gasifier (IBG), and the gas stream that passed through the catalyst bed was analyzed on-line using Fourier transform infrared spectrometry (FT-IR). In addition, the product gas was sampled periodically by collecting samples in gas bags for later analysis by gas chromatography (GC). A module for containing a catalyst bed was fabricated and flanged to the top of the IBG reactor. Operated in the fluidized mode, the fully instrumented IBG was used to pyrolyze and gasify coal. The gas and tar produced exited the reactor through the catalyst module containing a heated catalyst (NiSMM or dolomite) bed, passed through two water-cooled condensers, and was analyzed by on-line FT-IR. Trapped liquids were collected from the reactor following each test and were saved for later analysis. The catalyst was recycled to determine whether catalytic activity could be regained.

3.3 Reactor System

The IBG is a small batch process gasifier, with a charge capacity of nominally 70 g of coal. This unit provides data on the effects of bed fluidization, conversion of feedstock, reaction rate response to temperature, pressure, catalyst and feed gas composition and flow rate, and gaseous products, while providing sufficient quantities of conversion products for subsequent analysis. The top of the reactor has been fitted with a catalyst module through which the hot exhaust gas must pass before entering the series of two condensers. Although the module has no heaters of its own,

it receives heat from the reactor and tends to remain predictably within 50°–100°C of the reactor. A typical catalyst charge to the module is 30–50 g. Gas flows uninterrupted through the system and through the heated FT-IR cell. Gas exiting the second condenser flows through the cell where it is analyzed. The data obtained indicate the effect on the tar by measuring the levels of methane in the gas stream.

4.0 RESULTS

4.1 Cracking with Synthetic Nickel-Substituted Mica Montmorillonite (NiSMM)

North Dakota leonardite was heated in the IBG to 700°C in a 30% vol/vol H₂ atmosphere and the gaseous products, including tars, were passed through a bed of NiSMM catalyst, through a series of two traps, and then through a heated FT-IR gas cell as described above. Experimentation with the NiSMM ceased when FT-IR spectra containing a strong band at 2055 cm⁻¹ characteristic of nickel carbonyl, an extremely toxic gas, were observed. Since the molar absorptivity of nickel carbonyl is not known precisely, the graph of absorbance versus elapsed gasification time shown in Figure 1 includes the CO curve from the test with no catalyst as well as the traces assigned to nickel carbonyl.

4.2 Gas Production During Steam Gasification of Beulah Lignite

Table 2 shows the operating parameters for steam gasification of Beulah West Pit lignite in the IBG at temperatures selected on the basis of potential operating temperatures of various gasifiers. The conversions shown are based on moisture- and ash-free (maf) proximate analysis values for volatiles and fixed carbon in the raw coal sample. A clear conversion trend is evident, with 90 wt% conversion or above occurring at or above 700°C. Each reaction was carried out at

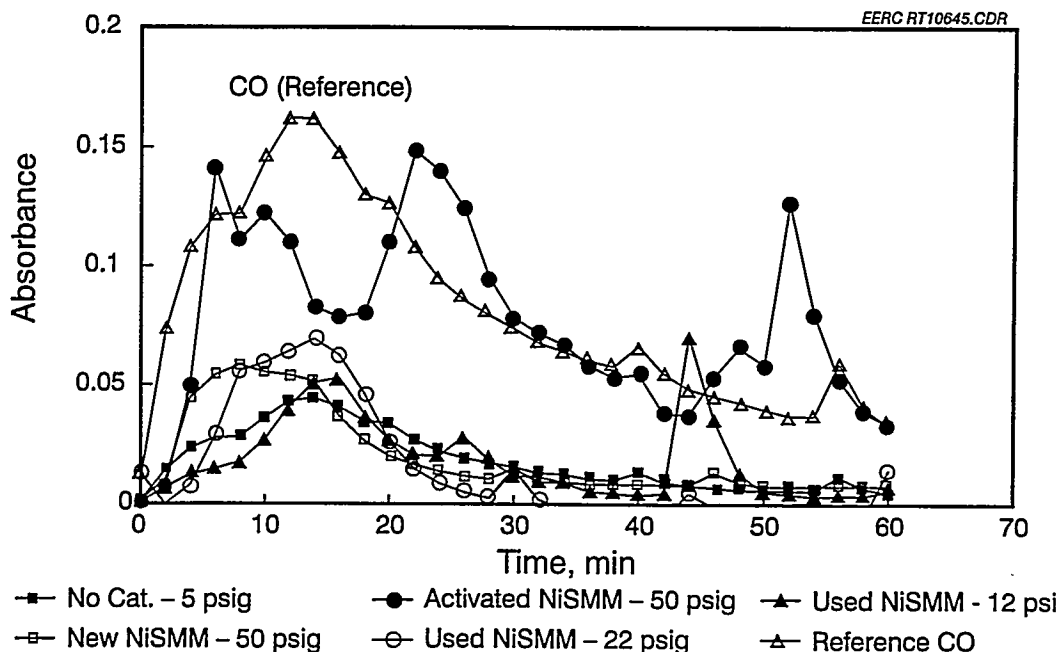


Figure 1. Spectral data as a function of time from gasification reactions showing IR absorbance at 2055 cm⁻¹ alleged to be nickel carbonyl. CO curve is shown for reference only.

TABLE 2

Conversion of Volatiles and Fixed Carbon to Tar and Gaseous Products Under Steam Gasification
Conditions at Different Temperatures for a Lignite and a Subbituminous Coal

Run No.	Coal	Temperature, °C	Catalyst	Atm, g/min at 50 psig	Conversion, wt% (mf)
IBG118	Beulah West	800+	Dolomite	Steam, 3-4	97
IBG119	Beulah West	250	Dolomite	Steam, 3-4	17
IBG120	Beulah West	550	Dolomite	Steam, 3-4	48
IBG121	Beulah West	700	Dolomite	Steam, 3-4	86
IBG122	Beulah West	400	Dolomite	Steam, 3-4	31
IBG123	Beulah West	250	Zeolite	Steam, 3-4	12
IBG124	Beulah West	700	Zeolite	Steam, 3-4	82
IBG125	Beulah West	700	Zeolite	Steam, 3-4	86
IBG126	Beulah West	550	Zeolite	Steam, 3-4	44
IBG127	Beulah West	800+	Zeolite	Steam, 3-4	98
IBG128	Beulah West	400	Zeolite	Steam, 3-4	34
IBG129	Beulah West	800+	None	Steam, 3-4	98
IBG130	Beulah West	250	None	Steam, 3-4	11
IBG131	Beulah West	700	None	Steam, 3-4	86
IBG132	Beulah West	550	None	Steam, 3-4	45
IBG133	Beulah West	400	None	Steam, 3-4	28
IBG134	Beluga	800	None	Steam, 3-4	88
IBG135	Beluga	800	Dolomite	Steam, 3-4	90
IBG136	Beluga	800	Zeolite	Steam, 3-4	87

the gasification temperature indicated until the production of CO₂ as monitored by FT-IR became negligible, generally 1 to 3 hours. The dolomite tended to decrepitate, producing fines, some of which blew over into the primary trap. The quantities of dolomite blown over did not correlate with temperature, but rather the fines tended to blow over with the occasional random increases in gas flow resulting primarily from uneven steam flow.

Three tests were also carried out with Beluga Alaskan subbituminous coal at 800°C, one each with no catalyst, with dolomite, and with zeolite. The results parallel those of the Beulah lignite tests at 800°C.

The methane content of the gaseous product normalized to the volatiles content of the coal from tests at each of the five gasification temperatures is shown in Figure 2. Pyrolysis methane is produced initially at temperatures above 500°C and drops off after about 25 minutes into the run.

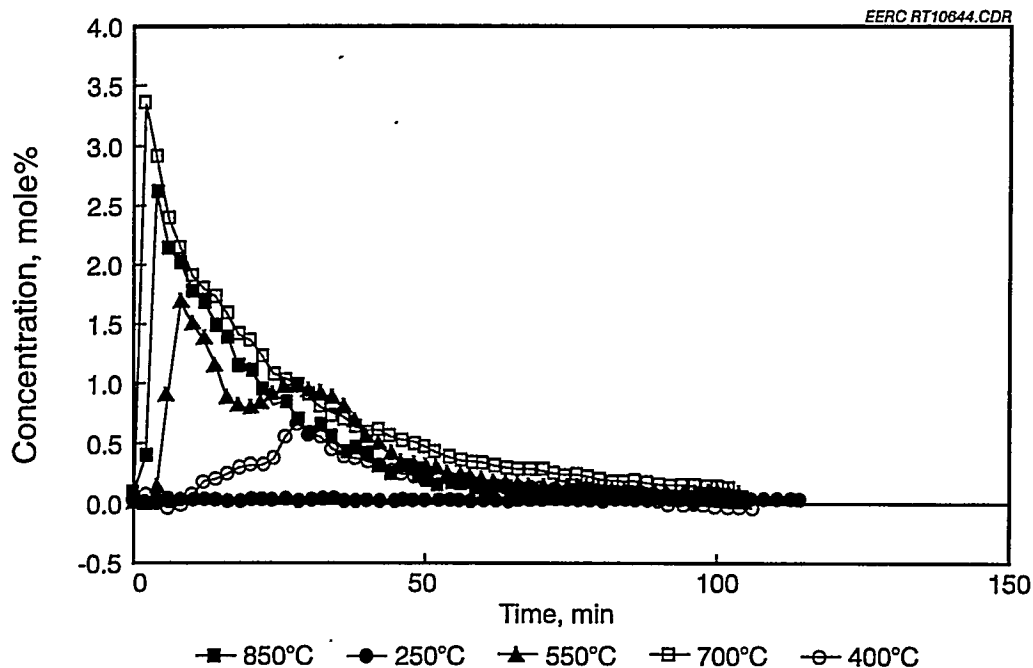


Figure 2. Methane concentration relative to tar production at each of five gasification temperatures for Beulah lignite.

Methane continues to be produced as a result of the methanation reaction and catalytic cracking. Methane is not a product of the reaction carried out at 250°C, but substantial methane is produced at each of the other temperatures. Indeed, at 700°C, more methane relative to the volatiles content was produced than at 850°C.

4.3 Tar Production During Steam Gasification of Beulah Lignite

The tar collected from each of the tests listed in Table 2 was analyzed following collection of the tar from the tubing and extraction from the liquids collected in the condensers. Table 3 shows the tar content collected following the catalyzed tar-cracking experiments (Tar_c) at each of the five temperatures, relative to the tar content collected following the uncatalyzed tar-cracking experiments (Tar_u) at each of the same temperatures. During each of these experiments, the catalyst was heated by the reactor and the flowing gases to approximately 50°–100°C cooler than the reactor temperature shown in Table 3. Dolomite decrepitation and powder carryover contributed to the unexpectedly high dolomite tar recovery at 700°C. Subsequently, care was taken during the remaining tests to ensure that this effect was minimized. Examination of the tar recovered from the 800+°C test showed a small amount of particulate material, probably dolomite in origin. Noticeable amounts of particulates were not found in the remaining tar samples.

TABLE 3

Tar Remaining from Steam Gasification of Beulah Lignite After Catalytic
Cracking Relative to Tar Remaining Without Catalytic Cracking, wt%

Temperature, °C	(Tar _c /Tar _w) 100% ¹	
	Dolomite	Zeolite
250	97	106
400	24	50
550	12	35
700	47	35 ¹
800+	19	32

¹ Average of two tests.

The tar was characterized by simulated distillation using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector (FID). Separation of the components was achieved with a DB-1 60-meter capillary column and with a hydrogen carrier gas flow of ~1 cm³/min. The oven was programmed for a temperature ramp of 2°C/min to 40°C, then 8°C/min to 320°C. The 1-μL injection of sample was split 1:50, i.e., ~2% of the injection went on column, with the remainder being vented. The approximate relative component concentrations were determined from the area of the gas chromatogram peaks. The area was calculated as a percentage based on area counts exclusive of solvent peak area. This calculation assumes equal response factors for all components detected. No attempt was made to identify individual components, but they were assumed to be an array of the usual hydrocarbons.

Plots of chromatography cumulative peak area% versus retention time for simulated distillations of tars collected from the tar-cracking tests with and without catalyst are shown as Figures 3-5. Tar produced during steam gasification at 800+ °C undergoes some thermal cracking even without the benefit of cracking catalyst, as shown in Figure 3, due to the thermolabile properties of alkylated compounds and the catalytic properties of the fly ash and steel reactor. Lighter organics with boiling points of approximately 150°C and 175°C constituted > 50% of the area of the recorded component peaks of the tar produced at 800+ °C. Based on component distributions, the tars produced at 400°, 550°, and 700°C, as determined by percentage area, were not readily distinguishable from one another. The lighter organics with boiling points of approximately 150° and 175°C made up approximately 40 area% of the gas chromatographable components produced at 400°, 550°, and 700°C.

The effluent gas stream passed through a dolomite bed contains few tar components that boil in the range 200° to 375°C, as shown by Figure 4. This result compares with 25-30 area% of the tar over the same temperature range when not subjected to contact with a catalyst bed (shown in Figure 3). The tars from each of the four tests with dolomite show a large area percentage for components boiling at a temperature > 375°C. The rest of the components have boiling points below approximately 225°C.

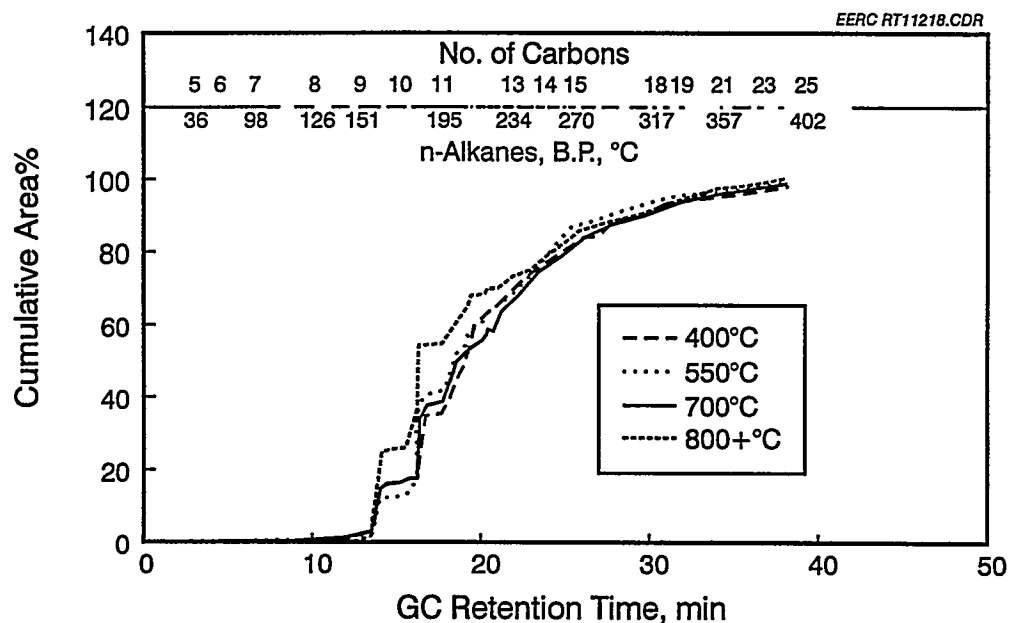


Figure 3. Simulated distillation of tar collected during gasification of Beulah lignite at 400°, 550°, 700°, and 800+°C.

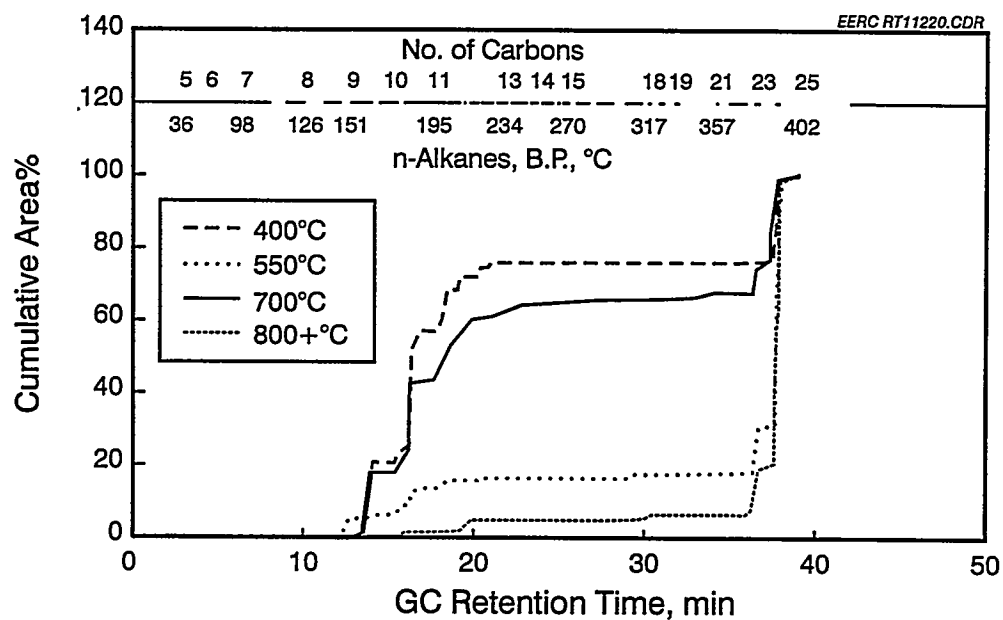


Figure 4. Simulated distillation of dolomite-cracked tar collected during gasification of Beulah lignite at 400°, 550°, 700°, and 800+°C.

Tar produced at 550°C and passed through a zeolite bed at approximately 450°–500°C had approximately 55% of its organic components in the boiling point range equal to or less than 175°C, as shown by Figure 5. Tar produced at 700°C and passed through a zeolite bed at approximately 600°–650°C had greater than 60 area% representing components with boiling points of approximately 175°C or less. Tar components in the same boiling point range produced during an 800+°C gasification test and passed through a bed of zeolite at 700°–750°C were represented by less than 50 area%. Components boiling at <270°C were represented by 60 area% of the 800+°C tar plot.

4.4 Tar Production During Steam Gasification of Beluga Subbituminous Coal

Tests at one temperature were carried out on Beluga subbituminous coal to determine the effectiveness of dolomite and zeolite in cracking tar produced from this coal during steam gasification in the IBG. The decrease in tar condensate through catalytic tar cracking was determined from data obtained at 800°C gasification of the subbituminous coal. Dolomite was shown to be more effective in cracking the tar than the zeolite at this temperature. When gas chromatography results and tar yield were compared, the area% and weight of the tar collected after cracking with zeolite were 58 area% and approximately one-half the weight of the tar produced without cracking catalyst. The same comparison between dolomite-cracked tar and tar from a test with no catalyst resulted in a dolomite-cracked tar yield of 28 area% and approximately one-fourth the weight of tar produced without cracking catalyst. In addition, the chromatograms show that dolomite gives a greater number of components than zeolite.

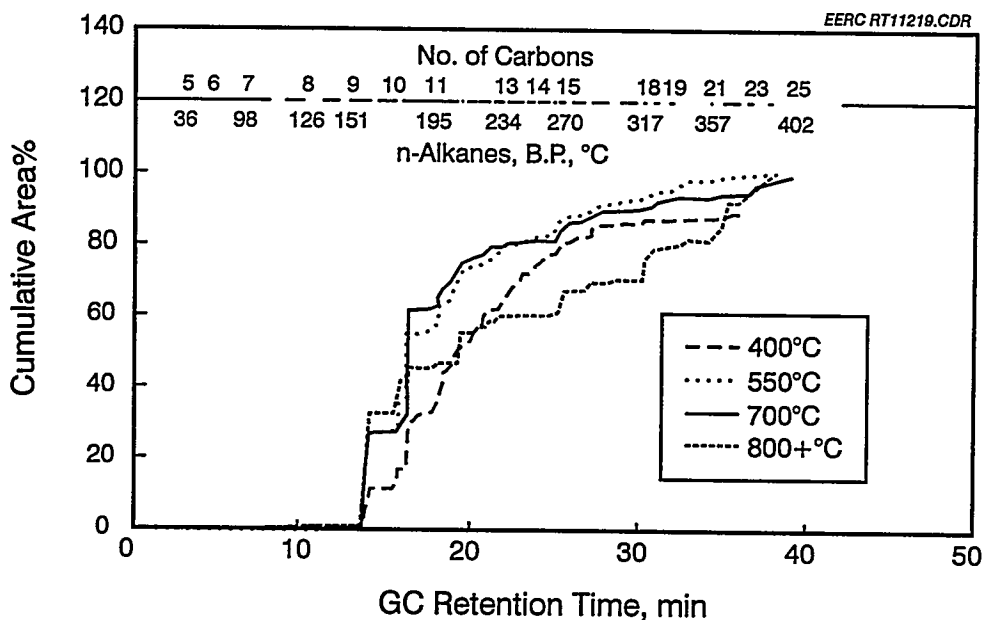


Figure 5. Simulated distillation of zeolite-cracked tar collected during gasification of Beulah lignite at 400°, 550°, 700°, and 800+°C.

4.5 Effect of Catalytic Cracking on Gas Production During Steam Gasification of Beulah Lignite

Gas samples were collected at 7, 14, 24, 48, 70, and 105 minutes during each test, and the gas was analyzed on a Hewlett-Packard 5880a GC configured as a refinery gas analyzer (0.45×60 molecular sieve and Porapak columns). Gas data at each time interval from the dolomite-catalyzed and the zeolite-catalyzed tar-cracking were compared with those data obtained from identical tests without tar-cracking catalyst. Particular attention was paid to hydrogen and total small hydrocarbon (C_1 to C_5) content. Calculations made on a nitrogen-free (fluidization gas) basis are reported in Tables 4, 5, and 6.

When normalized to the gas from a test without cracking catalyst, hydrogen content of the product gas was greater in the stream from the dolomite-catalyzed than from the zeolite-catalyzed tar-cracking tests carried out at 700° and 800°C. Although the zeolite was at nominal temperatures of 600–650°C and 700–750°C when the gasifier is at 700° and 800°C, respectively, it appeared to retain catalytic effect, i.e., it retained the ability to adsorb H_2 as in surface catalysis of hydrogenation reactions.

The average hydrogen content of the streams from the dolomite-catalyzed and the zeolite tar cracking were about the same for the 550°C test. The hydrogen content of the stream from the zeolite-catalyzed tar cracking was less than that of the dolomite-catalyzed tar cracking at 700°C. This result is probably due to the higher hydrogen absorptivity of zeolite. Zeolite, being a better hydrogenation catalyst than dolomite, promotes increased small hydrocarbon (C_1 to C_5) content of the product gases at 700° and 800°C. At 550° and 400°C, the hydrocarbon content of the gas stream from the dolomite-catalyzed tar cracking was generally higher than that of the zeolite-catalyzed tar cracking. In comparing dolomite tar cracking at the five temperatures, the greatest number of small hydrocarbon species were found at 550°C. Similarly with the zeolite, the greatest number of small hydrocarbon species were found in the 550°C test, but more species were found with zeolite than with dolomite at that temperature. At 400°C, the concentration of hydrocarbon species in the product gas of the dolomite-catalyzed tar cracking reaction is higher than that of the zeolite-catalyzed reaction, with methane being the only species of measurable concentration.

At 250°C, no methane was detected in the gas from the zeolite-catalyzed cracking of Beulah lignite tars, whereas a measurable amount was detected throughout the test in the reaction with the dolomite catalyst.

5.0 CONCLUSIONS

- Owing to the potential for production of extremely toxic nickel carbonyl gas, care must be exercised in the use of a NiSMM catalyst for cracking tars at high temperatures in reducing atmospheres such as those produced by coal gasification.
- Fifty percent or more of tar produced during steam gasification of Beulah lignite at temperatures of 400°–800+ °C is cracked by either dolomite or zeolite where the temperature of the catalyst is 50°–100°C below that of the reactor.

TABLE 4

Composition of Gas Produced from Steam Gasification of Beulah Lignite Coal with Dolomite Tar Cracking (mol%, nitrogen-free basis)

Composition, mol%	Time, min					
	7	14	24	48	70	105
Run Temperature, 800°C						
Hydrogen	59.9	68.3	69.0	53.4	40.0	35.8
Carbon Dioxide	23.0	25.2	27.3	43.3	56.2	59.7
Hydrogen Sulfide	0.2	0.1	0.0 ¹	0.0	0.0	0.0
Ethylene	0.5	0.2	0.1	0.0	0.0	0.0
Ethane	0.2	0.1	0.0	0.0	²	
Oxygen-Argon	7.5	1.0	0.1	1.5	2.3	4.5
Methane	5.9	2.8	1.7	0.8	0.8	3.7
Carbon Monoxide	2.7	2.3	1.8	0.9	0.5	0.0
Total Hydrocarbon	6.5	3.0	1.7	0.8	0.8	3.7
Run Temperature, 700°C						
Hydrogen	55.4	56.6	62.2	64.8	64.8	61.7
Carbon Dioxide	30.7	33.4	33.0	32.1	30.5	29.4
Propylene	0.1	0.1	0.0	0.0	0.0	0.0
Hydrogen Sulfide	0.2	0.1	0.0	0.0	0.0	0.0
Ethylene	0.3	0.2	0.0	0.0	0.0	0.0
Ethane	0.3	0.2	0.0	0.0	0.0	0.0
Oxygen-Argon	1.3	1.3	0.2	0.4	2.6	7.0
Methane	6.6	4.6	2.4	1.5	1.1	1.0
Carbon Monoxide	5.1	3.5	2.0	1.2	0.9	0.6
Total Hydrocarbon	7.3	5.1	2.4	1.5	1.1	1.0
Run Temperature, 550°C						
Hydrogen	18.5	20.1	31.1	45.6	66.2	52.4
Propane	0.2	0.0	0.0	0.0	0.0	0.0
Propylene	0.8	0.6	0.0	0.0	0.0	0.0
<i>iso</i> -Butane						

TABLE 4 (continued)

Composition, mol%	Time, min					
	7	14	24	48	70	105
Run Temperature, 550° (continued)						
<i>n</i> -Butane						
Hydrogen Sulfide						
<i>I</i> -Butene						
Ethylene	1.1	0.9	0.0	0.0	0.0	0.0
Ethane	1.9	1.7	1.4	0.0	0.0	0.0
Oxygen-Argon	5.3	9.6	11.3	7.0	15.4	20.4
Methane	17.4	17.2	18.4	15.2	12.3	12.6
Carbon Monoxide	17.0	16.0	14.0	9.5	6.8	5.8
Total Hydrocarbon	21.4	20.4	19.8	15.2	12.3	12.6
Run Temperature, 400°C						
Hydrogen	2.5	0.8	2.0	1.5	30.8	0.2
Carbon Dioxide	73.8	68.8	56.9	27.7	9.2	0.2
Propylene	0.0	0.0	0.0	0.0	0.0	0.0
Ethylene	0.0	0.0	0.0	0.0	0.0	0.0
Ethane	0.0	0.0	0.0	0.0	0.0	0.0
Oxygen-Argon	14.9	14.2	14.7	47.7	55.4	99.8
Methane	0.0	4.6	13.7	10.8	0.2	0.0
Carbon Monoxide	7.9	11.2	11.8	7.7	0.0	0.0
Total Hydrocarbon	0.0	4.6	13.7	10.8	0.2	0.0
Run Temperature, 250°C						
Hydrogen	0.0	0.0	0.0	4.8	2.8	6.3
Carbon Dioxide	0.0	0.0	0.0	0.0	0.0	0.0
Oxygen-Argon	0.2	97.6	95.2	76.2	25.0	75.0
Methane	0.0	1.5	1.0	1.0	1.1	2.5
Carbon Monoxide	0.0	0.0	0.0	0.0	0.0	0.0
Total Hydrocarbon	0.0	1.5	1.0	1.0	1.1	2.5

¹ 0.0 indicates peak area was less than detection limit.² Absence of number indicates no peak was present.

TABLE 5

Composition of Gas Produced from Steam Gasification of Beulah Lignite Coal
with Zeolite Tar Cracking (mol%, nitrogen-free basis)

Composition, mol%	Time, min					
	7	14	24	48	70	105
Run Temperature, 800°C						
Hydrogen	55.9	55.8	53.6	60.9	61.4	49.3
Carbon Dioxide	29.0	31.7	35.8	31.1	23.9	8.3
Hydrogen Sulfide	0.2	0.2	0.1	0.0	0.0	0.0
Ethylene	0.2	0.2	0.1	0.0	0.0	0.0
Ethane	0.1	0.1	0.0	0.0	0.0	0.0
Oxygen-Argon	0.6	0.6	2.1	1.2	5.1	4.1
Methane	4.6	3.1	1.8	1.8	3.1	2.3
Carbon Monoxide	9.3	8.4	6.5	4.9	5.7	10.1
Total Hydrocarbon	4.9	3.4	1.9	1.8	3.1	2.3
Run Temperature, 700°C						
Hydrogen	26.4	52.8	57.8	61.3	62.0	62.9
Carbon Dioxide	31.7	33.7	33.9	33.7	34.2	31.3
Propylene	0.9	0.2	0.1	0.0	0.0	0.0
Hydrogen Sulfide	0.6	0.3	0.1	0.0	0.0	0.0
Ethylene	1.8	0.4	0.1	0.0	0.0	0.0
Ethane	1.7	0.3	0.1	0.0	0.0	0.0
Oxygen-Argon	4.8	0.1	0.9	1.6	1.1	2.4
Methane	16.8	7.0	3.7	1.6	1.2	1.3
Carbon Monoxide	14.4	5.2	3.2	1.7	1.5	1.6
Total Hydrocarbon	21.2	7.9	4.0	1.6	1.2	1.3
Run Temperature, 550°C						
Hydrogen	14.2	7.5	40.0	55.0	41.9	33.3
Carbon Dioxide	48.5	10.1	30.5	25.7	16.7	10.0
Propane	0.3	0.0	0.0	0.0	0.0	0.0
Propylene	1.8	0.3	0.2	0.0	0.0	0.0

TABLE 5 (continued)

Composition, mol%	Time, min					
	7	14	24	48	70	105
Run Temperature, 550°C (continued)						
<i>iso</i> -Butane	0.1	0.0	0.0	0.0	0.0	0.0
<i>n</i> -Butane	0.1	0.0	0.0	0.0	0.0	0.0
Hydrogen Sulfide	1.0	0.3	0.0	0.0	0.0	0.0
<i>I</i> -Butene	0.3	0.0	0.0	0.0	0.0	0.0
Ethylene	2.0	0.3	0.4	0.0	0.0	0.0
Ethane	1.7	0.5	0.8	0.0	0.0	0.0
Oxygen-Argon	0.7	72.1	0.8	3.2	29.3	48.7
Methane	13.6	4.6	14.4	9.6	7.6	6.7
Carbon Monoxide	15.4	4.3	11.5	4.8	2.5	0.0
Total Hydrocarbon	20.0	5.6	15.9	9.6	7.6	6.7
Run Temperature, 400°C						
Hydrogen	0.3	1.5	3.9	6.5	37.6	10.3
Carbon Dioxide	10.1	73.5	67.3	32.6	9.9	0.0
Propylene	0.0	0.6	1.3	0.0	0.0	0.0
Ethylene	0.0	0.0	0.0	0.0	0.0	0.0
Ethane	0.0	0.0	0.0	0.0	0.0	0.0
Oxygen-Argon	88.6	9.7	2.6	23.9	5.9	72.4
Methane	1.6	2.6	9.2	17.4	5.0	10.3
Carbon Monoxide	0.8	10.9	13.1	8.7	2.0	6.9
Total Hydrocarbon	1.6	3.2	10.5	17.4	5.0	10.3
Run Temperature, 250°C						
Hydrogen	0.0	0.0	0.0	0.0	0.0	2.4
Carbon Dioxide	8.6	10.1	16.7	6.9	0.0	0.0
Oxygen-Argon	89.2	85.9	70.8	89.7	78.9	85.4
Methane	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	0.0	0.0	0.0	0.0	0.0	0.0
Total Hydrocarbon	0.0	0.0	0.0	0.0	0.0	0.0

TABLE 6

Composition of Gas Produced from Steam Gasification of Beulah Lignite Coal
with No Tar Cracking Catalyst (mol%, nitrogen-free basis)

Composition, mol%	Time, min					
	7	14	24	48	70	105
Run Temperature, 800°C						
Hydrogen	60.2	60.4	60.3	63.0	70.4	46.4
Carbon Dioxide	26.7	29.8	32.9	32.0	24.0	14.3
Hydrogen Sulfide	0.1	0.1	0.0	0.0	0.0	0.0
Ethylene	0.2	0.1	0.1	0.2	0.0	0.0
Ethane	0.1	0.0	0.0	0.0	0.0	0.0
Oxygen-Argon	0.8	0.8	0.4	0.4	2.0	9.3
Methane	3.8	2.0	1.6	1.5	0.7	0.3
Carbon Monoxide	7.8	6.7	5.0	2.7	1.6	0.8
Total Hydrocarbon	4.1	2.2	1.7	1.7	0.7	0.4
Run Temperature, 700°C						
Hydrogen	48.0	60.4	62.6	64.0	63.4	63.7
Carbon Dioxide	29.9	32.1	32.0	32.7	32.5	30.6
Propylene	0.1	0.0	0.0	0.0	0.0	0.0
Hydrogen Sulfide	0.4	0.1	0.0	0.0	0.0	0.0
Ethylene	0.3	0.0	0.0	0.0	0.0	0.0
Ethane	0.3	0.0	0.0	0.0	0.0	0.0
Oxygen-Argon	5.2	0.3	0.3	0.4	2.0	1.5
Methane	9.2	4.2	2.4	1.5	1.2	1.1
Carbon Monoxide	6.4	2.8	1.8	1.3	0.9	0.7
Total Hydrocarbon	9.9	4.2	2.4	1.5	1.2	1.1
Run Temperature, 550°C						
Hydrogen	3.6	13.5	31.1	10.9	51.8	42.6
Carbon Dioxide	69.4	47.7	33.9	9.0	24.5	14.2
Propane	0.4	0.0	0.0	0.0	0.0	0.0
Propylene	0.4	0.6	0.2	0.0	0.0	0.0

TABLE 6 (continued)

Composition, mol%	Time, min					
	7	14	24	48	70	105
Run Temperature, 550°C (continued)						
<i>iso</i> -Butane	0.0	0.0	0.0	0.0	0.0	0.0
<i>n</i> -Butane	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Sulfide	1.0	0.6	0.9	0.0	0.0	0.0
<i>l</i> -Butene	0.0	0.0	0.0	0.0	0.0	0.0
Ethylene	0.5	1.0	0.4	0.0	0.0	0.0
Ethane	0.6	1.8	0.9	0.0	0.0	0.0
Oxygen-Argon	3.1	1.7	1.9	72.5	7.9	12.9
Methane	7.2	16.6	17.3	4.6	10.1	6.5
Carbon Monoxide	13.6	16.3	12.8	2.2	5.0	0.0
Total Hydrocarbon	9.1	19.9	18.8	4.6	10.1	6.5
Run Temperature, 400°C						
Hydrogen	6.1	0.7	3.3	6.9	5.9	5.7
Carbon Dioxide	43.5	68.8	69.4	50.0	21.6	17.1
Propylene	0.0	0.0	0.0	0.0	0.0	0.0
Ethylene	0.0	0.0	0.0	0.0	0.0	0.0
Ethane	0.0	0.0	0.0	0.0	0.0	0.0
Oxygen-Argon	23.9	17.7	3.8	13.8	13.7	68.6
Methane	0.0	1.4	4.3	12.1	11.8	0.0
Carbon Monoxide	3.0	9.4	11.0	10.3	0.0	0.0
Total Hydrocarbon	0.0	1.4	4.3	12.1	11.8	0.0
Run Temperature, 250°C						
Hydrogen	0.9	0.0	0.0	0.0	0.0	0.0
Carbon Dioxide	13.6	34.0	25.0	8.1	28.6	0.0
Oxygen-Argon	81.8	60.4	71.4	24.3	57.1	16.3
Methane	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	0.0	0.0	0.0	0.0	0.0	0.0
Total Hydrocarbon	0.0	0.0	0.0	0.0	0.0	0.0

- Dolomite decrepitated during heating, especially at temperatures $>550^{\circ}\text{C}$, resulting in loss to downstream collection devices.
- Overall, dolomite was more effective in the lignite tar cracking, but the zeolite appeared to give slightly better results with the very heavy ends (tars) produced at the higher temperatures.
- The zeolite appeared to retain catalytic capacity even when heated to temperatures higher than normally thought to deactivate it.
- The zeolite retained its structural integrity even when used at $700^{\circ}\text{--}750^{\circ}\text{C}$.

6.0 RECOMMENDATIONS

- Optimize the temperature at which zeolite maximizes tar cracking.
- Optimize the catalyst bed depth.
- Examine catalyst tar cracking as a function of pressure.
- Investigate catalytic tar cracking of high- and low-volatile coals including bituminous coal.

7.0 PAPERS PRESENTED

The following papers relating to this work were presented:

Timpe, R.C.; Kulas, R.W.; Hauserman, W.B.; Sharma, R.; Olson, E.S.; Willson, W.G.
 "Catalytic Gasification of Coal for the Production of Fuel Cell Feedstock,"
Proceedings of the 10th World Hydrogen Energy Conference, Block, D.L.; Veziroglu, T.N.; Eds.; 1994 Vol. 2, pp 843–852.

Timpe, R.C.; Kulas, R.W.; Young, B.C. "Applications of Thermal Analysis Techniques in Support of Gasification Research," *In Proceedings of the 23rd NATAS Conference*; Toronto, Ontario, Canada, Sept. 25–28, 1994; pp 242–247.

Timpe, R.C.; Young, B.C. "A Comparison of a Zeolite and Dolomite as Gasification Tar Cracking Catalysts," *Prep. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1995**, 40 (4), 783–787.



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