

A COMPARISON OF ZEOLITE AND DOLOMITE AS GASIFICATION TAR-CRACKING CATALYSTS

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ABSTRACT

Unconverted liquid products produced during steam gasification of coal are heavy tars. The object of this study was to compare a zeolite with dolomite as tar-cracking catalysts. Up to 75% of the tars from a lignite and a subbituminous coal were cracked to lower molecular weight compounds by use of a heated catalyst bed. Collection of the tars downstream of the catalyst bed resulted in approximately 50% less tar from the test with dolomite as the catalyst than with zeolite. Simulated distillations of the tars showed more effective cracking with the dolomite than with the zeolite.

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 adsorption 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, e.g., 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 processes involving gas stream cleanup. Aerosol tars are not readily removed from gas streams by conventional means and, as a consequence, often result in plugged filters or fouled fuel cells, turbines, or sorbents. Catalytic cracking of tars to molecular moieties of C_{10} or smaller would prevent these problems. 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 IGCC system, provided tar generation and wastewater contamination can be minimized. This study involved 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.

EXPERIMENTAL

Two low-rank coals (LRC) were chosen for testing the tar-cracking propensity of dolomite and a zeolite (Engelhard X-2388). The proximate analyses of the Beulah West Pit lignite and Beluga Alaskan subbituminous are shown in Table 1.

Pyrolysis and steam gasification were carried out in the integrated bench-scale gasifier (IBG). A module for containing a catalyst bed was fabricated and connected by flange to the top of the IBG reactor. The module was heated through contact with the reactor (conduction) and flow-through of gases from the reactor (convection). 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 hot catalyst (dolomite or zeolite) bed, passed through two water-cooled condensers, and was analyzed by on-line Fourier Transform infrared spectrometry (FT-IR). Trapped liquids were collected in two water-cooled condensers connected in series and were saved for later analysis. In addition, the product gas was sampled periodically by collecting samples in gas bags for later analysis by gas chromatography (GC).

IBG

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 noting the levels of methane in the gas stream. In this study, dolomite and zeolite were tested for their effect on the pyrolysis tar.

RESULTS

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. The temperatures at which the Beulah lignite was gasified were selected on the basis of potential operating temperatures of various gasifiers. Beluga subbituminous coal was gasified at only one temperature, i.e., 800°C. The conversions shown are based on maf proximate analysis values for volatiles and fixed carbon in raw coal sample. There was a clear conversion trend with temperature, with 90 wt% conversion or above occurring at or above 700°C. Each reaction was carried out at the gasification temperature indicated until the production of CO₂ as monitored by IR spectrometry 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.

The methane content of the gaseous product normalized to the volatiles content of the coal from tests at each of the five gasification temperatures are shown in Figure 1. Pyrolysis methane is produced initially at temperatures above 500°C and drops off after about 25 minutes into the run. Methane continues to be produced as a result of 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.

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 and was 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. Care was taken following 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.

Characterization of the tar was by simulated distillation. This technique was carried out on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector (FID). A column and a hydrogen carrier gas flow at ~1 cm³/min was used to separate the components. The temperature ramp was 2°C/min to 40°C, then 8°C/min to 320°C. The 1 µl injection was split 1:50. Peak area % was calculated from area counts exclusive of solvent peak and was used to approximate relative component concentrations. No attempt was made to identify individual components, but they were assumed to be primarily 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 at the temperatures of the tests are shown as Figures 2-4. Tar produced during steam gasification at 800+°C undergoes some thermal cracking without benefit of cracking catalyst, as shown in Figure 2. Lighter organics with boiling points of approximately 150°C and 175°C constituted >50 area% of gas chromatographic components of the tar produced at 800+°C. The component distributions of the tars produced at 400°, 550°, and 700°C as determined by area% were not readily distinguishable. The lighter organics with boiling points of approximately 150° and 175°C made up approximately 40 area% of the gas chromatographic components produced at 400°, 550°, and 700°C.

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

Tar Production During Steam Gasification of Beluga Subbituminous Coal

The reduction in tar quantity by zeolite and dolomite tar-cracking catalysts was determined from data obtained at 800°C gasification of Beluga subbituminous coal using the IBG. Dolomite was shown to be more effective in cracking the tar than the zeolite. The bulk tar collected after cracking with zeolite was 58 gas chromatographic area% and approximately one-half the weight of the tar collected with no cracking catalyst, as compared with 28 gas chromatographic area% and approximately one-fourth the weight for cracking with dolomite. In addition, the chromatograms showed greater total components with dolomite than with zeolite.

CONCLUSIONS

- 50% 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.
- Dolomite decrepitated during heating, especially at the temperatures > 550°C, resulting in loss to downstream collection devices.
- Overall, dolomite was more effective in the lignite tar cracking, but the X-2388 zeolite appeared to give slightly better results with the very heavy ends (tars) produced at the higher temperatures.

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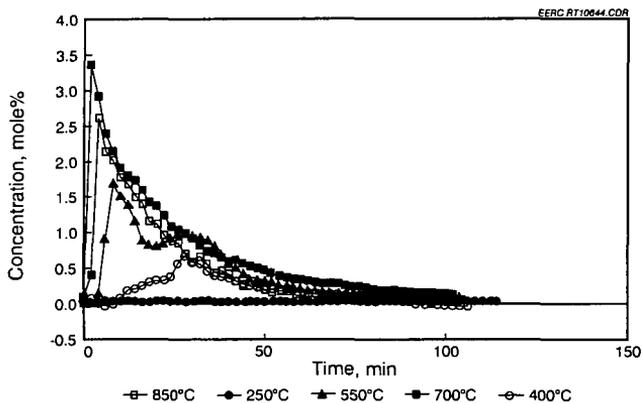


Figure 1. Methane concentration relative to tar production at each of five gasification temperatures.

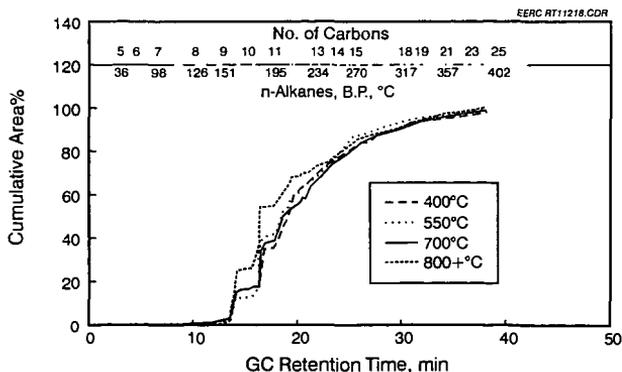


Figure 2. Simulated distillation of tar collected during gasification of Beulah lignite at 400°, 550°, 700° and 800 + °C.

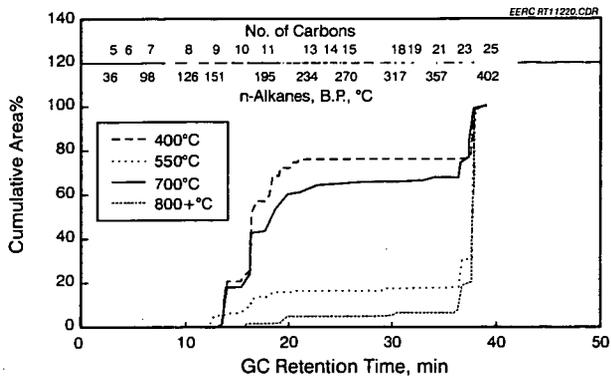


Figure 3. Simulated distillation of dolomite-cracked tar collected during gasification of Beulah lignite at 400°, 550°, 700°, and 800+°C.

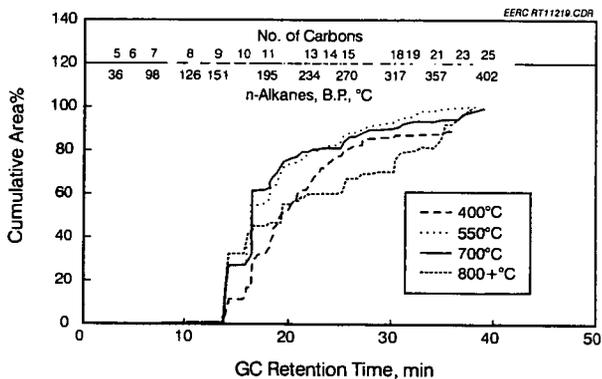


Figure 4. Simulated distillation of zeolite-cracked tar collected during gasification of Beulah lignite at 400°, 550°, 700°, and 800+°C.

TABLE 1

Proximate Analysis of Beulah West Pit Lignite and Beulah Subbituminous				
Coal	Moisture, AR, wt%	Volatiles, mf, wt%	Fixed Carbon, mf, wt%	Ash, mf, wt%
Beulah West Pit	30.2	44.8	47.6	7.6
Beluga (Alaskan)	22.3	45.0	44.5	10.5

TABLE 2

Conversion of Volatiles and Fixed Carbon to Tar and Gaseous Products
under Steam Gasification Conditions at Different Temperatures

Run No.	Coal	Temperature, °C	Catalyst	Atm., g/min at 50 psig	Conversion wt%, mf
IBG11	Beulah West	800+	Dolomite	Steam, 3-4	97
IBG11	Beulah West	250	Dolomite	Steam, 3-4	17
IBG12	Beulah West	550	Dolomite	Steam, 3-4	48
IBG12	Beulah West	700	Dolomite	Steam, 3-4	86
IBG12	Beulah West	400	Dolomite	Steam, 3-4	31
IBG12	Beulah West	250	Zeolite	Steam, 3-4	12
IBG12	Beulah West	700	Zeolite	Steam, 3-4	82
IBG12	Beulah West	700	Zeolite	Steam, 3-4	86
IBG12	Beulah West	550	Zeolite	Steam, 3-4	44
IBG12	Beulah West	800+	Zeolite	Steam, 3-4	98
IBG12	Beulah West	400	Zeolite	Steam, 3-4	34
IBG12	Beulah West	800+	None	Steam, 3-4	98
IBG13	Beulah West	250	None	Steam, 3-4	11
IBG13	Beulah West	700	None	Steam, 3-4	86
IBG13	Beulah West	550	None	Steam, 3-4	45
IBG13	Beulah West	400	None	Steam, 3-4	28
IBG13	Beluga	800	None	Steam, 3-4	88
IBG13	Beluga	800	Dolomite	Steam, 3-4	90
IBG13	Beluga	800	Zeolite	Steam, 3-4	87

TABLE 3

Uncracked Tar
(Tar_c/Tar_s)(100%)

Temp., °C	Dolomite	Zeolite
250	97	106
400	24	50
550	12	35
700	47	35*
800+	19	32

* Average of two tests.