Catalytic Gasification of Coal using Eutectic Salt Mixtures

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By
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CATALYTIC GASIFICATION OF COAL USING EUTECTIC SALT MIXTURES

Report for the Period
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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY
UNDER CONTRACT NUMBER DE-FG26-97FT97263 - 01
The Gas Research Institute (GRI) estimates that by the year 2010, 40% or more of U.S. gas supply will be provided by supplements including substitute natural gas (SNG) from coal. These supplements must be cost competitive with other energy sources. Large-scale commercial plants to produce SNG from coal will need to be constructed around the turn of the century to meet these projected demands. Currently, proven so-called first generation technologies for coal gasification include moving-bed Lurgi Pressure Gasification Process, Entrained-Bed Koppers-Totzek Process, and the Fluidized-Bed Winkler Process. The most suitable for large-scale SNG production is the Lurgi Process at Sasol II and III and at the Great Plains Coal Gasification Plant. The relatively newer technologies that have the potential for SNG manufacture include KBW (Westinghouse) Ash Agglomerating Fluidized-Bed, U-Gas Ash Agglomerating Fluidized-Bed, British Gas Corporation/Lurgi Slagging Gasifier, Texaco Moving-Bed Gasifier, and Dow and Shell Gasification Processes. These processes are at various stages of development, ranging from demonstration units to commercial demonstration units. However, the relatively newer technologies have several disadvantages such as high severities of gasification conditions, low methane production, high oxygen consumption, inability to handle caking coals, and unattractive economics.

The objectives of this study are to: identify appropriate eutectic salt mixture catalysts for coal gasification; assess agglomeration tendency of catalyzed coal; evaluate various catalyst impregnation techniques to improve initial catalyst dispersion; evaluate effects of major process variables (such as temperature, system pressure, etc.) on coal gasification; evaluate the recovery, regeneration and recycle of the spent catalysts; and conduct an analysis and modeling of the gasification process to provide better understanding of the fundamental mechanisms and kinetics of the process.

A review of the collected literature was carried out. The catalysts which have been used for gasification can be roughly classified under the following five groups: alkali metal salts; alkaline earth metal oxides and salts; mineral substances or ash in coal; transition metals and their oxides and salts; and eutectic salt mixtures. Studies involving the use of gasification catalysts have been conducted. However, most of the studies focused on the application of individual catalysts. Only two publications have reported the study of gasification of coal char in CO$_2$ and steam catalyzed by eutectic salt mixture catalysts. By using the eutectic mixtures of salts that show good activity as individual compounds, the gasification temperature can be reduced possibly with still better activity and gasification rates due to improved dispersion of the molten catalyst on the coal particles. For similar metal/carbon atomic ratios, eutectic catalysts were found to be consistently more active than their respective single salts. But the exact roles that the eutectic salt mixtures play in these are not well understood and details of the mechanisms remain unclear. The effects of the surface property of coals and the application methods of eutectic salt mixture catalysts with coal chars on the reactivity of gasification will be studied.

Based on our preliminary evaluation of the literature, a ternary eutectic salt mixture consisting of Li- Na- and K- carbonates has the potential as gasification catalyst. To verify the literature reported, melting points for various compositions consisting of these three salts and the temperature range over which the mixture remained molten were determined in the lab. For
mixtures with different concentrations of the three salts, the temperatures at which the mixtures were found to be in complete molten state were recorded. The results are as follows:

<table>
<thead>
<tr>
<th>Li$_2$CO$_3$ (Gm)</th>
<th>Na$_2$CO$_3$ (Gm)</th>
<th>K$_2$CO$_3$ (Gm)</th>
<th>Temperature Range (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>0.66</td>
<td>0.70</td>
<td>695-700</td>
</tr>
<tr>
<td>0.50</td>
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<td>0.30</td>
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As shown above, by increasing the amount of Li$_2$CO$_3$, the melting temperature range was reduced significantly. In the literature, the eutectic mixtures of Li- Na- and K-carbonates are claimed to have a lower activation energy than that of K$_2$CO$_3$ alone and they remain molten at a lower temperature than pure K$_2$CO$_3$. The slow increase in the gasification rates with eutectics reported in the literature is believed to be due to a gradual penetration of the coals and coal char particles by the molten and viscous catalyst phase. The even spreading of the salt phase seems to increase the overall carbon conversion rate.

In the next reporting period, a number of eutectic salts and methods of their application on the coal will be identified and tested.
1.0 INTRODUCTION

The Gas Research Institute (GRI) estimates that by the year 2010, 40% or more of U.S. gas supply will be provided by supplements including substitute natural gas (SNG) from coal. These supplements must be cost competitive with other energy sources. Large-scale commercial plants to produce SNG from coal will need to be constructed around the turn of the century to meet these projected demands. Currently, proven so-called first generation technologies for coal gasification include moving-bed Lurgi Pressure Gasification Process, Entrained-Bed Koppers-Totzek Process, and the Fluidized-Bed Winkler Process. The most suitable for large-scale SNG production is the Lurgi Process at Sasol II and III and at the Great Plains Coal Gasification Plant. The relatively newer technologies that have the potential for SNG manufacture include KBW (Westinghouse) Ash Agglomerating Fluidized-Bed, U-Gas Ash Agglomerating Fluidized-Bed, British Gas Corporation/Lurgi Slagging Gasifier, Texaco Moving-Bed Gasifier, and Dow and Shell Gasification Processes. These processes are at various stages of development, ranging from demonstration units to commercial demonstration units. However, the relatively newer technologies have several disadvantages such as high severities of gasification conditions, low methane production, high oxygen consumption, inability to handle caking coals, and unattractive economics.

To resolve these problems, studies involving the use of gasification catalysts have been conducted. However, most of the studies focused on the application of individual catalysts and little research attention has been given to the use of eutectic salt mixtures as catalysts. An advantage offered by the use of eutectic catalysts in coal gasification is that a lower temperature can be employed. Besides lower gasification severity and increased methane yield, other advantages of catalytic coal gasification include (Gallagher and Euker, 1979): elimination of slagging problems in the gasifier since oxygen injection for heat input is not required; the reduction of the caking tendency of bituminous coals by the catalysts; lack of tars and oils production which, coupled with the low gasifier effluent temperature, permit the recovery of high level heat from the gasifier effluent (the absence of tars also simplify acid gas removal and water cleanup); separate shift and methanation reactors are unnecessary since all methane is formed in the gasifier (in addition, the use of large fluid-bed gasifiers result in high output per gasifier); and minimization of materials and mechanical problems due to moderate reaction temperature and pressures in the gasifier.

It has been shown (Radovic et al, 1983 and Lang, 1982) that the initial catalyst dispersion and subsequent catalyst distribution during gasification are important problems that hinder the development of economically competitive commercial coal gasification. Catalyst application techniques which provide poor catalyst contact with the coal and, therefore, low catalyst dispersion result in poor catalyst performance. In this study, we propose to identify suitable low melting eutectic salt mixtures and application techniques for improved coal gasification.

2.0 OBJECTIVES

The objectives of this study are to: identify appropriate eutectic salt mixture catalysts for coal gasification; assess agglomeration tendency of catalyzed coal; evaluate various catalyst impregnation techniques to improve initial catalyst dispersion; evaluate effects of major process
variables (such as temperature, system pressure, etc.) on coal gasification; evaluate the recovery, regeneration and recycle of the spent catalysts; and conduct an analysis and modeling of the gasification process to provide better understanding of the fundamental mechanisms and kinetics of the process.

3.0 TEHNCIAL APPROACH

To meet the project objectives the proposed work has been subdivided into the following tasks.

Task 1 Selection of Eutectic Salt Mixtures: literature review; identification of appropriate eutectic salt mixtures; evaluation of catalyst application methods; and TGA studies to evaluate gasification characteristics.

Task 2 Evaluation of Gasification Performance in a Bench-scale, Fixed-bed Reactor: evaluation of catalyst dispersion; study of the effects of process variables on the performance of gasifiers; and evaluation of the recovery, regeneration and recycle of the catalysts.

Task 3 Data Analysis and Reporting: data analysis and modeling; economic evaluation of the gasification process; and project management and reporting.

4.0 SUMMARY OF SIX MONTHS ACCOMPLISHMENTS

4.1 Task 1: Selection of Eutectic Salt Mixtures

4.1.1 Literature Review

A review of the collected literature was carried out. The catalysts which have been used for gasification can be roughly classified under the following five groups: alkali metal salts; alkaline earth metal oxides and salts; mineral substances or ash in coal; transition metals and their oxides and salts; and eutectic salt mixtures.

A. Alkali Metal Salts. The catalysis of coal and carbon gasification by alkali metal salts is a well-known phenomenon. Although the mechanism of alkali catalysis has been the subject of a large body of research, it is still not well understood. In particular, the active form of the alkali catalyst under gasification conditions has been the subject of a great deal of speculation and controversy. Steam and CO$_2$ gasification catalyzed by alkali-metal salts are similar in a number of aspects, such as increased reactivity with better catalyst dispersion (Mims et al., 1982), higher alkali metal carbon ratio and order of catalytic activity of alkali metals (Cs >Rb>K>Na>Li) (Moulijn and Kapteijn, 1986). The present state of knowledge of alkali-metal-catalyzed carbon gasification by CO$_2$ was summarized by Moulijn and Kapteijn(1987). Detailed reaction mechanisms are given by Cerfontain et al(1987).

The catalytic behavior of alkali metal carbonates (Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, Cs$_2$CO$_3$ and Rb$_2$CO$_3$) and oxides (Na$_2$O, Rb$_2$O, Cs$_2$O, Li$_2$O and K$_2$O) in graphite oxidation reaction were studied by McKee and Chatterji (1975). It was found that the catalytic effect involves an oxidation-reduction cycle with the intermediate formation of peroxide or higher oxide of the
alkali metal. The catalytic effect of alkali carbonates in the graphite-CO$_2$ reaction was explained on the basis of a different oxidation-reduction cycle involving the formation of free alkali metal as intermediate. K$_2$CO$_3$ increases steam and CO$_2$ gasification rate, permits the reaction to operate at low temperature for methanation, and inhibits swelling and agglomeration of caking coals. K-salts are highly mobile, easy to apply by dry mixing and can maintain a constant number of active sites by constant renewal. Considering the anion effect, carbonates, sulfates and nitrates are found to be better catalysts than the silicates and halides. K$_2$CO$_3$ is found to maintain the gasification rate even as carbon conversion increases to high level. The catalyzed reaction, which is rapidly accelerated at temperatures in the vicinity of the melting point of the alkali metal carbonate, occurs most readily in the presence of the lithium salt (McKee and Chatterji, 1978). The catalytic mechanism involves an oxidation-reduction cycle with the intermediate formation of the hydroxide of the alkali metal. Li-salts, especially Li$_2$CO$_3$ and LiOH, showed better catalytic activity due to their ability to reduce the apparent activation energy. However, activity of Li$_2$CO$_3$ is inhibited in the presence of CO and CO$_2$. In general, alkali-salts of weak acids made better catalysts except for phosphates, borates, and silicates which were likely to form polymeric, glassy compounds at the gasification temperature. Coating of the carbon surface by the polymeric compounds inhibited the reaction with the gas phase.

Further results of the gasification of graphite in carbon dioxide and water vapor have been achieved (McKee, 1982). The results show that lithium salts, specifically the carbonate and hydroxide, are the most active catalysts for both reactions. The oxysalts of the alkali metals are effective catalysts in the reaction of graphite with carbon dioxide and water vapor and can be explained on the basis of the participation of the catalyst in a cyclic series of elementary reactions. The details of the catalytic process depend on the temperature, the salts present, and the nature of the oxidizing gas. Spiro et al. (1984) used the microprobe to examine the alkali catalyst (Li$_2$CO$_3$ or K$_2$CO$_3$) particles during gasification of carbonaceous materials in CO$_2$ and steam. Both in CO$_2$ and steam, alkali catalysts showed evidence of mobility. Alkali carbonate catalysts achieve an apparently molten state during incipient gasification. For single crystal graphite, circular pitting, hexagonal pitting and channeling were observed.

Studies, of the steam gasification of coal char using alkali and alkaline-earth metal catalysts (Liu and Zhu, 1986), show that the order of catalytic activity is K$_2$SO$_4$ or K$_2$CO$_3$ > Na$_2$CO$_3$ > KCl > NaCl > CaCl$_2$ or CaO. The loading method of K$_2$CO$_3$ had little effect on its catalytic activity but that of CaO influenced the activity significantly. The kinetics of CO$_2$ gasification of carbon, catalyzed by Na, K, Rb and Cs was studied by Kaptejn et al (1986). It was found that the reaction rate is independent of the CO$_2$ pressure over a range of 4-30 bar, and increases with catalyst loading in the order Na < K < Rb < Cs. In the case of Na the number of active sites probably increases with temperature due to carbonate decomposition. Individual Na-salts such as NaCl, Na$_2$CO$_3$, and Na$_2$SO$_4$ were found to be less active than when used with other salts as a catalyst mixture. Chen and Yang (1997) reported that many types of intermediates have been proposed and intensively investigated for alkali catalyzed gasification reaction of carbon by CO$_2$ and H$_2$O. The proposed active intermediates for potassium include metallic K, K$_2$O, K$_2$O$_2$, K$_2$CO$_3$, and clusters that are nonstoichiometric compounds with excess metal.
B. Alkaline-Earth Metal Oxides and Salts. The reactivity of coal char towards steam is known to be enhanced by the presence of alkali and alkaline-earth metal salts or oxides. To overcome the expense and loss in recovery of K-salts, the cheaper Ca-salts were tried. They performed better at lower catalytic loadings but were immobile and needed to be chemically combined with the organic matter for high activity. In general, Ca-salts could not replace K-salts because of their loss of activity during gasification and their not being a good methanation catalysts. Most studies in this field on catalytic gasification of coals show that potassium salts (especially potassium carbonate) are the most active. Evaluations of the catalytic activity of alkaline-earth metal oxides, e.g. CaO, are not consistent. Apart from other properties of coals, it is believed that this inconsistency is related to different methods and conditions of catalyst loading on the coal.

The behavior of calcium as a steam gasification catalyst showed that the calcium compounds provide good catalytic activity under certain conditions (Lang and Neavel, 1982). Essentially, the calcium must be atomically dispersed throughout the char to obtain good activity. Calcium is poorly active unless it is very well dispersed by chemical reaction with the organic matter. Sufficient sites occur naturally in lower-rank coals, and some of these coals have undergone ion-exchange with calcium naturally. Radovic et al (1983) evaluated the importance of catalyst dispersion in the gasification of lignite chars. The relatively high gasification reactivity of lignite chars, compared to those obtained from higher rank coals, is due to the catalytic effect of the initially very highly dispersed CaO on the char surface. Char deactivation is caused primarily by CaO crystallite growth.

Ohtsuka and Tomita (1986) also carried out calcium-catalyzed steam gasification of Yallourn brown without demineralization and heat treatment. Calcium catalyst showed a high activity at ~950 K. Calcium hydroxide, carbonate, acetate, nitrate and chloride exhibited similar catalyst effectiveness. The gasification rate increased with increasing the calcium loading and at a loading of 5 wt %, complete gasification was attained within 25 minutes at 973 K. Comparison of uncatalyzed and catalyzed rates showed that calcium catalyst can lower the reaction temperature by 150 K. The impregnation of calcium salt on devolatilized char in place of raw coal resulted in the formation of rather large catalyst particles, and their activity was low. For calcium-catalyzed gasification reaction (Chen and Yang, 1997), the proposed active intermediates include CaCO$_3$, CaO, CaO$_2$ and Ca$_x$O$_y$.

An exploratory study was made to evaluate calcium as an inexpensive substitute for catalytic potassium in the Exxon SNG process (Lang and Neavel, 1980). Ca(OH)$_2$ was found to have good activity for the steam-carbon reaction, and was sometimes better than potassium because it reacted less with the coal mineral. Calcium appeared to be immobile and well dispersed and chemically reacted with the char to perform well. One disadvantage of calcium as a catalyst is that it tends to deactivate during gasification. This could be due to its immobility or its inability to re-associate chemically with char. In Jha and McCormick’s experiment (1992), calcium acetate was used as the catalyst precursor and added to the high sulfur Illinois Basin coal at the coal preparation plant. They showed that the catalyst could reduce swelling, capture sulfur and increase carbon conversion or lower the gasification temperature.
Effects of CaO, high-temperature treatment, carbon structure and coal rank on intrinsic char oxidation rates were investigated by Gopalakrishnan and Bartholomew (1996). Comparison of intrinsic oxidation rates of unloaded Spherocarb and (acid washed) chars showed a trend of increasing intrinsic rate with decreasing skeletal density suggesting that the intrinsic rate is a function of carbon structure. Studies of ion-exchange calcium from calcium carbonate and low-rank coals (Ohtsuka and Asami, 1996) show the extent of the exchange is dependent on the crystalline form of CaCO$_3$, and higher for aragonite naturally present in seashells and coral reef than for calcite from limestone. The exchanged Ca promotes gasification and achieves 40-60 fold rate enhancement for brown coal with a lower content of inherent minerals.

C. Transition and Other Metals, their Oxides and Salts. McKee (1985) also studied the rare earth oxides (La$_2$O$_3$, CeO$_2$, Eu$_2$O$_3$, Gd$_2$O$_3$, Sm$_2$O$_3$, Nd$_2$O$_3$, Yb$_2$O$_3$, and Tb$_2$O$_3$) as carbon oxidation catalysts. It was verified that only CeO$_2$ showed significant activity in accelerating the gasification of graphite by oxygen between 500 and 1000°C. Cerium salts (such as Ce$_2$(CO$_3$)$_3$, Ce$_2$(SO$_4$)$_3$, Ce(SO$_4$)$_2$, Ce(NO$_3$)$_3$, (NH$_4$)$_4$Ce(SO$_4$)$_4$, Ce(OH)$_2$, (NH$_4$)$_2$Ce(NO$_3$)$_6$ and Ce$_2$(C$_2$O$_4$)$_3$), which decompose to a finely dispersed oxide phase at low temperature were found to be very active catalysts. The metallic impurities were found to affect the gasification of graphite in water vapor and hydrogen (McKee, 1974). Iron, cobalt and nickel are active catalysts for the former reaction between 600-1000°C when the metal is kept in the reduced state by means of added hydrogen. Vanadium and molybdenum are weak catalysts under these conditions, whereas copper, zinc, cadmium, silver, chromium, manganese and lead are inactive. When hydrogen is absent so that the metal remains in the oxidized state, the catalytic activity of all these impurities is low or negligible.

McCarty and Wise (1979) investigated the nature of carbon deposits on Ni/Al$_2$O$_3$ by TPR with H$_2$ and identified seven carbon states. Kieffer and van der Baan(1982), using TPR with hydrogen on a coked Fe/ZnO catalyst, were also able to identify three carbon states of different reactivity. The characterization of coke deposits on Pt/Al$_2$O$_3$ reforming catalysts and studies of their reactivity have also been intensely researched. The gasification of carbon on the SiO$_2$-Al$_2$O$_3$ catalyst was not catalyzed. The carbon deposit on Pt/Al$_2$O$_3$ catalyst may be gasified at a lower temperature. Silva and Lobo (1986) carried out investigation of CO$_2$ gasification of activated carbon catalyzed by molybdenum oxide. They showed that MoO$_3$ is a good catalyst at low temperature and moderate pressures. The effect of loading on reactivity showed saturation above ~ 0.3 wt%.

The mechanism of CO$_2$ gasification of carbon catalyzed with group VIII metals was investigated by using steady-state gasification with thermogravimetric analysis (Ohme and Suzuki, 1996). Both steps in the oxidation and reduction of iron species proceeded very fast and the key step for carbon gasification was the oxidation step of iron metal in the redox cycle. The TPD spectra and XRD also clarified that the active species is highly dispersed iron metal and the deactivated species are sintered iron and highly oxidized iron. Tsujiet et al(1996) studied the coal gasification by using the ZnO/Zn redox system. A more effective chemical conversion was obtained via a proposed two-step scheme as compared to that obtained via the conventional single-step direct steam gasification. CO formation was more favorable with the coal-ZnO redox reaction than with the coal H$_2$O reaction in the 1173-1373 K temperature range. Catalytic activity of V$_2$O$_5$/γ-Al$_2$O$_3$ as a typical transition metal oxide catalyst was also measured for
comparison (Miyazaki et al., 1997). \( V_2O_5/\gamma-Al_2O_3 \) showed linear increase of achieved conversion with the amount of catalyst, although the catalytic turnover number was limited. The carbonate supported on LSCMP (\( La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.45}Pt_{0.05}O_3 \)) showed high conversion at an alkali metal to carbon ratio as low as 0.012. The carbonate supported on \( \gamma-Al_2O_3 \) and LSCMP alone showed very limited activity.

D. Mineral Substances or Ash in Coal. A TPD study of coal chars in relation to the catalysis of mineral matter shows that the presence of mineral matter is responsible for these gas evolutions (Kyotani, 1986). The exchanged metal species like Ca and Na significantly catalyzed the gasification reaction. Carbon-catalyzed exchange carbon and oxygen between carbon dioxide and potassium carbonate was researched at 500-1000K by Saber et al. (1984). Two labile surface carbonate complexes could be probable intermediates. The influence of mineral matter on the reactivity of chars derived from a bituminous coal during K-catalyzed steam gasification was carried out by Formella et al. (1986). They performed experiments with chars with different ash contents impregnated with different amounts of \( K_2CO_3 \) and subsequently gasified at 973 K and 4 MPa in pure steam.

Investigation of the mechanism of the alkali metal catalyzed gasification of carbon has shown that the most effective catalysts are generally the carbonates, oxides and hydroxides; other active salts tend to convert to these species under gasification conditions (McKee, 1983). Alkali intermediates may also interact with the substrate to form free radical or possibly interaction compounds. For a given additive (\( Li_2CO_3, Na_2CO_3, K_2CO_3, Cs_2CO_3 \) and \( Rb_2CO_3 \)), the magnitude of the catalytic effect increased with the rank of the parent coal (McKee et al., 1983). A progressive loss in catalytic activity on thermal cycling during steam gasification was associated with reaction of the alkali salts with mineral matter in the chars. Catalytic activity of metal carbonates was studied for the gasification of activated carbon grains at 673-773 K by supporting the carbonates on carbon, alumina, and a perovskite-type oxide (\( La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.45}Pt_{0.05}O_3 \), LSCMP).

E. Eutectic Salt Mixtures. Only two known publications on the use of eutectic salts are available. Choi (1983) reported that \( K_2CO_3, Na_2CO_3, CaCO_3 \), and other promising chemicals were used to identify relatively simple eutectic compositions. Some chemicals were mixed and heated to 1300°F in a muffle furnace. The mixtures showing partial melting in the experiment showed complete melting if their eutectic compositions were used. For example, the \( K_2CO_3 + Na_2CO_3 \) mixture, when mixed at the eutectic composition of 0.4 and 0.6 weight fractions, showed complete melting while the mixture of 0.5/0.5 weight fractions showed only partial melting. A dry mixture of \( K_2CO_3 /Na_2CO_3 /CaCO_3 \) prepared at 0.4/0.35/0.25 by weight resulted in complete melting.

The eutectic salt catalysts (\( NaCl, Li_2CO_3, Na_2CO_3, K_2CO_3, Na_2SO_4; Na_2Cl_2-Na_2CO_3, Na_2Cl_2-SO_4, KF-K_2CO_3, K_2CO_3-KCl, LiF-Li_2CO_3; Na_2Cl_2-Na_2CO_3-Na_2SO_4, Li_2CO_3-Na_2CO_3-K_2CO_3 \)) for graphite and coal char gasification have been studied by McKee et al. (1985). It has been found that low melting binary and ternary eutectics of the alkali metal halides, carbonates and sulfates are more effective low temperature catalysts for the \( CO_2 \) and steam gasification of graphite and coal chars than the pure salt components. The reduced melting points of the
eutectic phases result in enhanced catalytic activity at lower gasification temperature by achieving a better dispersion of salt phases on the substrates.

4.1.2 Identification of appropriate Eutectic Salt Mixtures

Based on the review of the phase diagrams of various eutectic mixtures (Roth et al., 1969), the systems shown in Table 1 have been identified for further investigation in this study. The chemicals and other accessories to enable us prepare the catalysts and catalyst loaded coal/char samples have been ordered. In addition, 10 lb of Illinois #6 coal have been ordered from the Penn State Coal Sample Bank for the project.

Based on our preliminary evaluation of the literature, a ternary eutectic salt mixture consisting of Li- Na- and K- carbonates has the potential as gasification catalyst. To verify the literature reported, melting points for various compositions consisting of these three salts and the temperature range over which the mixture remained molten were determined in the lab. For these mixtures with different concentrations of the three salts, the temperatures at which the mixtures were found to be in complete molten state were recorded. The results are as follows:

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<th>Temperature Range (F)</th>
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<td>0.70</td>
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As shown above, by increasing the amount of Li₂CO₃, the melting temperature range was reduced significantly. In the literature, the eutectic mixtures of Li- Na- and K-carbonates are claimed to have a lower activation energy than that of K₂CO₃ alone and they remain molten at a lower temperature than pure K₂CO₃. The slow increase in the gasification rates with eutectics reported in the literature is believed to be due to a gradual penetration of the coals and coal char particles by the molten and viscous catalyst phase. The even spreading of the salt phase seems to increase the overall carbon conversion rate.

4.1.3 Evaluation of Catalyst Application Methods

To identify the best catalyst loading technique and to ensure high catalyst dispersion, the incipient wetness technique, ion exchange, and low- and high-temperature soaking method are being evaluated as catalyst application methods for the gasification of coal char in CO₂ and steam.

4.1.4 TGA Experimental Setup to Evaluate Gasification Characteristics

The existing thermogravimetric analyzers (TGA) at Clark Atlanta University (CAU) have been set up and will be used to conduct the atmospheric pressure gasification studies in steam and in CO₂ to evaluate the gasification of the coal samples catalyzed by the eutectic salts. The gasification temperature will be kept at about 200-1100°C. The TGA studies will be used to
<table>
<thead>
<tr>
<th>No</th>
<th>Eutectic Salt Mixtures Mol %</th>
<th>Melting Temp. °C</th>
<th>No</th>
<th>Eutectic Salt Mixtures Mol %</th>
<th>Melting Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.5%Cs$_2$CO$_3$-82.5%CsNO$_3$</td>
<td>380</td>
<td>25</td>
<td>~56%Li$_2$SO$_4$-44%CdSO$_4$</td>
<td>~560</td>
</tr>
<tr>
<td>2</td>
<td>3.6%K$_2$CO$_3$-96.4%KNO$_3$</td>
<td>326</td>
<td>26</td>
<td>~80%Li$_2$SO$_4$-20%CaSO$_4$</td>
<td>~700</td>
</tr>
<tr>
<td>3</td>
<td>9.3%K$_2$CO$_3$-90.7%KOH</td>
<td>367</td>
<td>27</td>
<td>64%Li$_2$SO$_4$-36%MnSO$_4$</td>
<td>~580</td>
</tr>
<tr>
<td>4</td>
<td>94%K$_2$CO$_3$-6%K$_2$SO$_4$</td>
<td>355</td>
<td>28</td>
<td>~58%Li$_2$SO$_4$-42%PbSO$_4$</td>
<td>~640</td>
</tr>
<tr>
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<td>32</td>
<td>~46%Na$_2$SO$_4$-54%ZnSO$_4$</td>
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<td>9</td>
<td>8.3%Na$_2$CO$_3$-91.7%NaOH</td>
<td>285</td>
<td>33</td>
<td>~55%Rb$_2$SO$_4$-45%MgSO$_4$</td>
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<td>10</td>
<td>42%CaCO$_3$-58%CaSO$_4$</td>
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<td>34</td>
<td>~12%Na$_2$SO$_4$-88%V$_2$O$_5$</td>
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<tr>
<td>11</td>
<td>58%Na$_2$CO$_3$-42%Rb$_2$CO$_3$</td>
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<td>35</td>
<td>~62%K$_2$SO$_4$-38%V$_2$O$_5$</td>
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<td>12</td>
<td>87%Li$_2$CO$_3$-13%Li$_2$O</td>
<td>705</td>
<td>36</td>
<td>42.9%Li$_2$CO$_3$-57.1%K$_2$CO$_3$</td>
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<tr>
<td>17</td>
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<td>19</td>
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<td>42.4%LiNO$_3$-57.8%KNO$_3$</td>
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<td>249.91</td>
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<tr>
<td>22</td>
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<td>460</td>
<td>46</td>
<td>1.9Sr(NO$_3$)$_2$-98.1LiNO$_3$</td>
<td>250.77</td>
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<td>~598</td>
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<td>~62%KNO$_3$-38%CsNO$_3$</td>
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<td>191</td>
<td>48</td>
<td>~58%NaNO$_3$-42%CsNO$_3$</td>
<td>190</td>
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</table>
select the appropriate reaction conditions such as residence time and temperature for coal gasification in the fixed-bed reactor. The thermograms generated from the TGA experiments will be useful for the assessment of the effectiveness of the catalyst loading techniques and the behavior of the eutectic salts during pyrolysis and gasification of the coal. The TGA studies will also be used to evaluate the kinetics and the mechanism of the gasification reaction.

4.2 Bench Scale High-Pressure Fixed-Bed Gasification System

The bench scale high pressure fixed bed gasification system has been assembled to experimentally evaluate the effect of various process variables on the performance of the selected catalyst system. At present, it is being used to study the catalytic steam gasification of poultry wastes and necessary changes will be made later on for our process study.

5.0 PLANS FOR THE NEXT SIX-MONTH PERIOD

Only two publications have reported the study of gasification of coal char in CO$_2$ and steam catalyzed by eutectic salt mixture catalysts. By using the eutectic mixtures of salts that showed good activity as individual compounds, the gasification temperature can be reduced possibly with still better activity and gasification rates due to improved dispersion of the molten catalyst on the coal particles. For similar metal/carbon atomic ratios, eutectic catalysts were found to be consistently more active than their respective single salts. But the exact roles that the eutectic salt mixtures play in these are not well understood and details of the mechanisms remain unclear. The effects of the surface property of coals and the application methods of eutectic salt mixture catalysts with coal chars on the reactivity of gasification have not been studied. The behavior and application techniques of binary and ternary salt mixtures and the process conditions will be initiated in our lab.

5.1 Identification of Appropriate Eutectic Salt Mixtures

The available eutectic salt mixtures under gasification conditions will be identified. Samples of the salts will be placed in a muffle furnace at various temperatures and in N$_2$ atmosphere to determine their melting ranges. Eutectic salts that have melting points in the 200-800°C range will be selected for the gasification studies. To determine the caking or agglomeration properties, samples of a bituminous coal will be ground to various sizes and mixed with the selected eutectic salts. The free swelling index (the agglomeration tendency) of the coal and its samples containing the salts will be determined using the ASTM D720-91 method. This method has been successfully applied to coals containing sodium and calcium catalysts.

5.2 Evaluation of Catalyst Application Methods

The major thrust of this aspect of the project is to identify the best catalyst loading technique that will ensure high catalyst dispersion. The catalyst addition methods that have been applied in previous studies include mixing of the dry catalyst precursors with coal, the incipient wetness technique, ion exchange, and low-and high-temperature soaking. Typically, after physically
mixing the catalyst with the coal, no further treatment is required before introduction of the coal into the gasifier. However, the sample may be dried at 100-120°C.

5.3 Study of the Surface Property of the Coal Char with/without Catalyst

The surface charge on the coals will be measured in aqueous solutions under well-controlled conditions of pH and ionic strength using a "Pen Kem Model 501 Lazer Zee Meter" zeta potential equipment available at Clark Atlanta University. Controlling the slurry pH will enhance the initial catalyst distribution in the coal and, hence, the surface charge and the efficiency of the exchange of the catalyst metal ions with exchangeable ions in the coal. Catalyst addition by low and high temperature soaking will also be evaluated. To enhance the effectiveness in identifying the best catalyst loading technique and to minimize trial-and-error or one-variable-at-a-time experiments, statistical experimental design methods will be used in this task. The effectiveness of the techniques to be studied will be compared to physical mixing of the solid catalysts with the coal. The initial assessment of the effectiveness of each technique will involve catalyst dispersion measurements on the impregnated coal samples using scanning electron microscope equipped with an energy dispersive x-ray (EDX) system to provide catalyst mapping. Ultimately, the effectiveness of the loading technique will be deduced from gasification rates and kinetics data.

5.4 TGA Study to Evaluate the Gasification Reaction

The TGA studies will be used to select the appropriate reaction conditions such as residence time and temperature for coal gasification in the fixed-bed reactor. The thermograms generated from the TGA experiments will be useful for the assessment of the effectiveness of the catalyst loading techniques and the behavior of the eutectic salts during pyrolysis and gasification of the coal. The TGA studies will also be used to evaluate the kinetics and the mechanism of the gasification reaction. These results will be compared to those obtained from the subsequent modeling and bench scale studies undertaken in this project.

5.5 Bench Scale High-Pressure Fixed-Bed Gasification System to evaluate the gasification of coal char with eutectic salt mixture catalysts.

Experiments will be carried out using bench scale high-pressure fixed-bed gasification system to test the operation of the unit. The candidate eutectic mixtures and their mode of application would first be identified from Task 1. Subsequently, a systematic fixed-bed gasification study will be initiated using the bench-scale, high-pressure fixed-bed gasification system.

6.0 REFERENCES:


Mckee, D. W. 1985, “Rare earth oxides as carbon oxidation catalysts”, Carbon, Vol.23(6), 707-713.


Roth, R. S., M. A. Clevinger and D. Mckenna 1964, “Phase Diagrams for Ceramists”, American Ceramic Society.


