CATALYTIC GASIFICATION OF COAL USING EUTECTIC SALT MIXTURES

Report for the period
April 1999 to October 1999

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ABSTRACT

This is the progress report for the DOE grant DE-FG26-97FT97263 entitled, *Catalytic Gasification of Coal Using Eutectic Salt Mixtures* for the period April 1999 to October 1999. The project is being conducted jointly by Clark Atlanta University, the University of Tennessee Space Institute and Georgia Institute of Technology. The overall objectives of the project 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 and system pressure) on coal gasification; evaluate the recovery, regeneration and recycle of the spent catalysts; and conduct thorough analysis and modeling of the gasification process to provide better understanding of the fundamental mechanisms and kinetics of the process.

During this reporting period, free swelling index measurements of the coal, fixed-bed gasification experiments, kinetic modeling of the catalyzed gasification, and X-ray diffraction analysis of catalyst and gasified char samples were undertaken.

The gasification experiments were carried out using two different eutectic salt mixtures of $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (LNK) system and $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (NK) system. The gasification process followed a Langmuir-Hinshelwood type model. At 10 wt % of catalyst loading, the activation energy of the ternary catalyst system (LNK) was about half (98kJ/mol) the activation energy of the single catalyst system (K_2CO_3), which is about 170 kJ/ mole. The binary catalyst system (NK) showed activation energy of about 201 kJ/mol, which is slightly higher, compared to the K_2CO_3 catalyst system. The ternary catalyst system was a much better eutectic catalyst system compared to the binary or single catalyst system. In general, a eutectic with a melting point less than the gasification temperature is a better substitute to the single alkali metal salts because they have good catalyst distribution and dispersion in the carbon matrix.

The free selling index of the coal was about 1.5 (1 to 2) in comparison to 2.5 (2 to 3) for the coal samples with ternary eutectic. The results for the raw coal were consistent with those from the Penn State Coal Bank. The XRD characterization showed unidentified peaks in the spectra of some of the samples and require further studies to draw any conclusions at the point.

Student continued to actively participate in the project at all three institutions. Ms. Godarvaty complete her masters degree on the project at the University of Tennessee Space Institute. A new graduate student has joined the project team at UTSI.

The project continues to be on schedule and has been making steady progress. The team meets regularly (every two months) at Clark Atlanta University to review the progress on all activities made.

1.0 INTRODUCTION AND OBJECTIVES

This progress report for the DOE grant DE-FG26-97FT97263 entitled, *Catalytic Gasification of Coal Using Eutectic Salt Mixtures* covers the period April 1999 to October 1999. The overall objectives of the project 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 and system pressure) on coal gasification; evaluate the recovery, regeneration and recycle of the spent catalysts; and conduct thorough analysis and modeling of the gasification process to provide better understanding of the fundamental mechanisms and kinetics of the process.

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

Task 1 Selection of Eutectic Salt Mixtures: This task involves 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: This task includes 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: This encompasses data analysis and modeling; economic evaluation of the gasification process; and project management and reporting.

A summary of the progress and accomplishments on the project tasks in the last six months is given below.

2.0 SUMMARY OF SIX MONTHS ACTIVITIES

2.1 Task 1: Selection of Eutectic Salt Mixtures

2.1.1 Materials

Coal was prepared from ground Illinois #6. Compositional data for the parent coal and for the char prepared from it are given in Table 1. The coal used in the lab was 60 mesh.

Table 1 Compositional data for Illinois No.6 coal (hv Cb rank)

Proximate analysis (wt %)		Ultimate analysis (wt %)	
H ₂ O	13.20	Ash	11.62
Ash	11.62	C	57.33
Volatiles	35.44	H	3.98
Fixed C	39.74	N	0.99
		S	4.80
		O	8.07

The salts investigated as catalysts and used for preparing the eutectic salts included Sigma Chemical Co. analytical reagent grade Rb_2CO_3 , Li_2CO_3 , Na_2CO_3 and K_2CO_3 . TGA gasification measurements were carried out in CO_2 (Holox Products).

2.1.2 Procedures

A Preparation of eutectic catalysts:

Ternary eutectic catalysts were prepared by fusion of finely ground salt mixtures having compositions corresponding to the eutectic melting temperatures, as obtained from published phase diagrams (1). Fusion was carried in air at temperatures at least 100°C above the respective eutectic melting points. After cooling, the solidified melts were crushed and finely ground in an agate mortar. The resulting glassy material was then crushed and added to coal in required amount.

B Bench Scale High Pressure High Temperature Fixed – Bed Gasification Unit

A SS-304 $\frac{3}{4}$ " diameter tube of 0.065" wall thickness was used as a reactor with a working design pressure greater than 1500 psi at 1400°F . It was randomly packed with ceramics beads, above which coal was placed in a stainless steel 200-mesh basket. A type-K thermocouple was used to measure the temperature of the bed. The reactor was heated using a long vertical furnace – SIB Lindberg Model 123. The water and inlet gases were preheated using a separate 4" long furnace – SIB Lindberg Model 123. The pressure was maintained in the reactor using a Tescom Industrial Controls Model 26-1726-24 back pressure regulator. The cooled gases passed through a Rockwell T-110 cumulative gas flowmeter to determine their total volume. The gas samples were analyzed in a SRC 8610C TCD type gas chromatograph (GC). Water was pumped against a back pressure of 800 psi into the preheater using a Dionex Model DQP-1 pump. The char samples were analyzed for their fixed carbon content before and after the gasification in a thermogravimetric analyzer – Perkin Elmer TGA 7.

The data from the gas chromatograph was analyzed using the 'PeakSimple' software and the resulting concentrations of various gaseous species were used to obtain the gasification rates and extent of conversion for each run.

The conversions based on TGA results were calculated using the formula below:

$$X_c = [(C_o - C)/C_o] * 100 \quad (1)$$

Where: C_o =Initial carbon content in the feed to gasifier (grams) and
 C =Final carbon content after gasification (grams)

The fixed bed reactor studies were undertaken at the University of Tennessee Space Institute.

C Kinetic Modeling for Binary and Ternary Catalyst Systems

Detailed analysis and kinetic modeling of the gasification process was undertaken based on the fixed-bed reactor at UTSI and the TGA studies at Clark Atlanta University. A generalized form of a Langmuir-Hinshelwood type expression for heterogeneous catalytic kinetics was applied to the gasification reaction. Details of the model may be found in the masters thesis of Godavarty (2).

D Method for Free-Swelling Index Test

D720-91 (ASTM Standard) was used to measure the free-swelling index of the coal at Clark Atlanta University. The test method consisted essentially of heating 1 g of coal, in a covered silica crucible in an oven. The oven was adjusted to give a temperature of 800 ± 10 °C, in 1.5 minutes, and 820 ± 5 °C, in 2.5 minutes. The heating was continued for not less than 2.5 minutes. The coke button obtained was compared with a series of standard outlines to get a value corresponding to that of the nearest outline.

One gram of ground 60 mesh coal was weighed in a cold crucible, and the crucible was lightly tapped 12 times on the bench, rotating it between taps, to level the surface of the coal. The crucible was then covered with a lid and placed upright in the oven.

Three buttons were made for each time sample of coal tested. The three coke buttons of each sample of coal being tested was viewed through the sight tube and compared to the series of standard profiles. The drawing with which the button was compared was placed exactly in the center of the field of vision from the top of the tube. The button was rotated around its axis until the maximum cross-section area was in line with the drawing and viewed with one eye placed immediately over the top of the tube.

E X-ray diffraction Experiments

Catalyst constituents, eutectic salts, pyrolyzed and gasified char samples were examined using x-ray diffractometry (XRD) at Georgia Institute of Technology. The purpose of these XRD studies was two-fold: (1) to determine if any phases or moieties are formed in the eutectic salts that are distinct from those present in the individual Li_2CO_3 , Na_2CO_3 , and K_2CO_3 salts, & (2) to establish changes in the XRD patterns of the eutectic salts before and after gasification reaction. Table 7 contains a list of the samples studied. Using a 2 hour scan period resulted in significantly improved signal to noise ratio over a 20 min scan. Hence all the samples listed in Table 7 were obtained using 2 hr. scans.

3.0 SUMMARY OF RESULTS AND DISCUSSION

3.1 Kinetic Modeling for ternary and binary catalyst systems

In our previous report, the results for several single salt catalysts and binary and ternary eutectic catalysts investigated at Clark Atlanta University were presented (3,4). The

eutectic catalysts increased gasification rate significantly. The methods of catalyst preparation and addition had significant effect on the catalytic activity and coal gasification. The catalytic activity increased by varying degrees with catalyst loading. Based on the Clark Atlanta University studies in the previous reporting period, the project team selected the 43.5% Li_2CO_3 -31.5% Na_2CO_3 -25% K_2CO_3 (LNK) 39% Li_2CO_3 -38.5% Na_2CO_3 -22.5% Rb_2CO_3 (LNR) ternary eutectic and the 29% Na_2CO_3 -71% K_2CO_3 (NK) binary eutectic for the fixed-bed studies at UTSI.

In our previous report, we also reported the studies on the LNK and NK catalysts in the bench scale fixed-bed reactor at UTSI. Based on the results obtained from the fixed-bed reactor, a study on the kinetic modeling for the eutectic salt mixtures as the gasifying catalyst was carried out at the University of Tennessee Space Institute.

Kinetics of catalytic steam gasification of coal/graphite has been studied extensively by many researchers at various operating conditions using different varieties of coal samples. All the models that were attempted to fit the experimental results were of the Langmuir-Hinshelwood type of rate expression for heterogeneous systems (5,6). The kinetics of K-catalyzed steam gasification was described using this model at Exxon Corporation in the 1980's (7) in a very extensive manner. Similar models including the effect of product gases like hydrogen have also been developed by Schumacher (5).

The kinetics of only a single-catalyst system was studied in detail in the past. Work on eutectics as catalysts started with the thermogravimetric studies by McKee in 1981. It was continued by Tetsuya in 1991, to study the behavior of eutectics on coal gasification in a quartz reactor. Tetsuya had dealt only with the synergistic effects of the gasification rates, when equimolar quantities of the catalyst components were used as binary catalyst systems. The present work can be considered as an expansion of the earlier work using eutectics by Tetsuya in the early 1990's and by McKee at General Electric in the mid 80's.

3.1.1 ASSUMPTIONS FOR THE KINETIC EXPRESSION

A Langmuir-Hinshelwood type of rate expression was used to fit the steam gasification rate data (5,6). Inhibition in the char consumption due to H_2 concentration was neglected. The linearity of the first order plots of $-\ln(1-X_c)$ as a function of gasification time illustrated in Figures 1 and 2 for LNK and NK catalyst systems indicate that the steam gasification probably followed first-order with respect to the unreacted char in the reactor bed. This is consistent with the earlier work with coal using various single alkali metal salts as catalysts (8,9).

In reality, the gasification reaction occurs thermally as well as catalytically. The overall gasification rates is given by:

$$[-dC/dt \text{ (overall)}] = [-dC/dt \text{ (cat)}] + [-dC/dt \text{ (thermal)}] \quad (2)$$

The thermal gasification is usually very small compared to the catalytic gasification. However, the kinetics of such mixed gasification cannot be determined easily. The effect of thermal gasification is seen clearly in Figure 3, where the linear fit shows an intercept that probably accounts for thermal gasification. For the first order reaction, the line should go through the origin. The non-zero intercept could be due to the transient of the system in following a step input of steam into the reactor. Hence the data were forced to fit reasonable lines through the origin, to simplify the kinetic expression and obtain a nearly first-order reaction. These linear fits are believed to be probably less than 10% different in slope from the slopes for the lines that did not pass through the origin.

The Langmuir-Hinshelwood expression is given by:

$$r/C_c = k_1 p(\text{H}_2\text{O}) / (1 + k_2 p(\text{H}_2\text{O})) \quad (3)$$

Where

k_1 corresponds to the reaction rate constant

k_2 is the absorption constant

r is the gasification rate of carbon in the bed (gm/min)

C_c is the remaining carbon in the bed at any instant time, t (gm)

r/C_c is the specific gasification rate (min^{-1}) and

$p(\text{H}_2\text{O})$ is the partial pressure of steam.

The rate constants, which are functions of temperature, are given by the following expressions,

$$k_1 = k_{10} \exp (-E_1/RT) \quad (4)$$

$$k_2 = k_{20} \exp (-E_2/RT) \quad (5)$$

Where, k_{10} and k_{20} are the frequency factors and E_1 and E_2 the activation energies of the gasification and absorption respectively. Equation 3 may be inverted to give a linear relationship from which the rate constants, k_1 and k_2 may be obtained from the slope and intercept. The calculated rate data from the experimental results for the different temperature conditions were used to obtain the rate expressions. The partial pressure of steam, $p(\text{H}_2\text{O})$ was calculated from the average moles of water/steam entering and leaving the bed at every instant of time, t .

The resulting linear plot following inversion of Equation 3 are shown in Figures 4 and 5 for the ternary (LNK) and binary (NK) catalyst systems respectively. The regressed values of the slopes and intercepts following equation 6 for the two catalyst systems, LNK and NK, are given in Table 2. From these values, the rate constants, k_1 and k_2 are obtained by simple algebra. These k_1 and k_2 values were then used to obtain the activation energies and frequency factors for the two catalyst systems from their Arrhenius plots. These plots are shown in Figures 6 and 7 respectively. The values of the activation energies and the frequency factors calculated from these plots are given in Table 3. From the calculated values of the activation energies, one can see that E_2 in both catalyst systems has a negative value, indicating that it is probably an adsorption

phenomenon, which would liberate heat in contrast to the water gas reaction, which requires heat for the reaction to occur.

The activation energy for the LNK eutectic catalyst system was found to be a little less than half the activation energy of the NK system. This shows that the gasification reaction is more favorable and better enhanced using the ternary catalyst system than the binary catalyst system. This difference could also be due to the liquid state of the LNK eutectic at the gasification temperature, which has a tendency to reduce the activation energy of the steam gasification reaction. The binary catalyst at gasification temperatures is in a solid solution state, requiring probably more activation energy for the catalyst to become active and well dispersed for increased gasification. The activation energy of the gasification reaction was apparently lower when the ternary was used as the catalyst (98.63 kJ/mol), in comparison to the literature reported value of 170kJ/mol of activation energy when 10 wt% of K_2CO_3 was used as the catalyst.

Table 2 The Slope and Intercept for the LNK and NK system at different temperatures

Catalyst	Temperature ($^{\circ}F$)	(k_2/k_1)	($1/k_1$)
LNK	1200	2818.7	186.64
LNK	1275	1300.5	15.251
LNK	1350	730.73	19.5
LNK	1420	651.93	1.4527
NK	1200	11390	569.06
NK	1350	875.79	22.137

Table 3 Rate parameters for steam gasification*

Catalyst/Parameter	k_{iO}	E_i (kJ mol $^{-1}$)
LNK / k_1	154.08 kPa $^{-1}$ min $^{-1}$	98.63
LNK / k_2	3.7x10 $^{-12}$ kPa $^{-1}$	-180.3
NK / k_1	32.835x10 6 kPa $^{-1}$ min $^{-1}$	201.5
NK / k_2	3.347x10 $^{-7}$ kPa $^{-1}$	-91.87

* $k_i = k_{iO} \exp(-E_i/RT)$

McKee made similar observations during the catalytic coal gasification experiments of coal using the eutectic salt mixtures in a TGA (5).

The Langmuir –Hinshelwood model for the two catalyst systems is given by:

For LNK catalyst system:

$$-\frac{dC}{dt} = \frac{154.08 \exp(-11863/T) p_{H_2O} \cdot C_c}{1 + [3.7 \times 10^{-12} \exp(21695/T) p_{H_2O}]} \quad (6)$$

for NK catalyst system:

$$-\frac{dC}{dt} = \frac{32.835 \times 10^6 \exp(-24241/T) p_{H_2O} \cdot C_c}{1 + [3.3477 \times 10^{-7} \exp(11050/T) p_{H_2O}]} \quad (7)$$

where

p_{H_2O} – partial pressure of steam (kPa)

C_c – Amount of carbon in the bed at any instant of time, t (gm)

T – Gasification temperature ($^{\circ}K$)

This calculated rate expression for each catalyst system was used to find the specific gasification rate at different steam flow rates and the results obtained were found to be close to the experimentally determined values. When this rate expression was being derived, the gasification rates at different temperature conditions were used to evaluate the values of the rate constants, k_1 and k_2 [i.e. using runs 1,2 3 and 10 for LNK system (Table 4) and runs 11,12 and 13 of the NK system (Table 5)]. These calculated values of k_1 and k_2 with their temperature dependency were used for the experimental runs carried out at different steam flow rates. The consistency of the experimental results with the derived model is shown in Figures 8 and 9 for the two catalyst systems. It is observed that the model over predicts the kinetics of the reaction at higher temperatures in both cases. This could be attributed to the fact that, for steam gasification at higher temperatures (say above 1380 $^{\circ}F$), the reaction rate may be more influenced/controlled by the pore- and inter-particle diffusion instead of chemical reactions (1).

Table 4 Experimental conditions for steam gasification runs using the LNK eutectic catalyst*

Run	Temperature ($^{\circ}F$)	Pressure (psig)	Catalyst loading (%)	Steam flow rate (ml/min)	Initial fixed carbon (%)
1	1200	50	10	0.213	68.43
2	1350	50	10	0.213	68.43
3	1420	50	10	0.213	68.43
4	1350	150	10	0.213	68.43
5	1350	300	10	0.213	68.43
6	1350	50	5	0.213	71.26
7	1350	50	15	0.213	62.54
8	1350	50	10	0.084	68.43
9	1350	50	10	0.145	68.43
10	1275	50	10	0.213	65.00

*Duration of gasification = 255 minutes

Initial char = 2.5 GMS in bed

The Langmuir-Hinshelwood model developed was thus used to fit the data for different steam flow rates and temperatures. However, it was not used to fit the data for the runs carried out at different catalyst loadings, because of insufficient data. Further experimentation is required at different temperatures for each catalyst loading to derive a similar expression for the rate constants.

Table 5 Schematic of the operating conditions for the catalytic coal gasification using the NK eutectic catalyst*

Run	Temperature (°F)	Catalyst loading (%)	Steam flow rate (ml/min)	Initial fixed carbon (%)
11	1200	10	0.23	60.32
12	1350	10	0.23	60.32
13	1420	10	0.23	60.32
14	1350	5	0.23	68.53
15	1350	15	0.23	55.1
16	1350	10	0.084	60.32
17	1350	10	0.143	60.32

*Initial char = 2.5 gms in the bed
Duration of gasification = 255 minutes
Reactor pressure = 50 psig

3.2 Free Swelling Index Studies

Free swelling is the property of certain coals when heated, without restraining influence, to expand freely in volume, as in the volatile matter test or when burned as fuel. The swelling number was determined as the number inscribed in the outline that the largest profile of the button most nearly matched according to Figure 10. The average swelling number of the series, expressed to the nearest 1/2 unit, was reported according to the ASTM method (10). Table 6 shows the results of the free swelling indexes for the tests performed. As the ternary catalysts were added to the coal at 10% wt, the indexes showed a little higher value than that of coal. This might be due to the catalysts accelerating the releasing of heat at high temperature at short time. The data gotten in our lab was very close to the data supplied by the Pennsylvania State coal bank.

3.3 XRD Characterization

The seven samples in Table 7 served as the base line or reference against which the eutectic salt samples and aged samples were examined. Figure 11 shows XRD spectra of Illinois No. 6 coal. The pattern matches that of graphite in the Reference Library in the XRD software. There are significant peaks at 27⁰, 32⁰, and 56⁰. We plan to confirm that

these peaks correspond to mineral matters present in the coal. Illinois No. 6 coal contains up to 5 % FeS₂, in addition to alumina and silica species.

Table 6 Free-Swelling Index of Samples

Coal	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Index	1.5	2	2	1.5	2	1.5
Average of Index	2			2		
Coal + Ternary catalysts	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Index	2.5	2.5	2.5	2.5	2	2.5
Average of Index	2.5			2.5		

Table 7 X-Ray Diffraction Samples

No.	Sample	Comments
1	Fresh Coal	Base-line
2	Na ₂ CO ₃	Base-line
3	Li ₂ CO ₃	Base-line
4	K ₂ CO ₃	Base-line
5	NaNO ₃	Base-line
6	NaOH	Base-line
7	KOH	Base-line
8	2.9 % Na ₂ CO ₃ + 7.1 % K ₂ CO ₃ + char	Gasified Char
9	10 % Li ₂ CO ₃ + char	Gasified Char
10	10 % K ₂ CO ₃ + char	Gasified Char
11	10 % Na ₂ CO ₃ + char	Gasified Char
12	43.5 % Li ₂ CO ₃ + 31.5 % Na ₂ CO ₃ + 25 % K ₂ CO ₃	Eutectic salt
13	10% Li-Na-K carbonate eutectic + pyro. coal	Pyrolyzed coal
14	(M1) Li-Na-K carbonate eutectic + pyro. coal	Pyrolyzed coal
15	(M1) Li-Na-K carbonate eutectic + char	Gasified Char
16	(B1) 0.22 % Na ₂ CO ₃ + 9.78 % NaNO ₃ + char	Gasified Char
17	(B2) 0.93 % K ₂ CO ₃ + 9.07 % KOH + char	Gasified Char
18	(B3) 9.4 % K ₂ CO ₃ + 0.6 % K ₂ SO ₄ + char	Gasified Char
19	(B4) 9.64 % KNO ₃ + 0.36 % K ₂ CO ₃ + char	Gasified Char
20	(B5) 9.17% NaOH + 0.83 % Na ₂ CO ₃ + char	Gasified Char

Figure 12 shows XRD spectra of the eutectic salt (Sample no. 12). Individual peaks are identified as those due to one or more of the three constituents (Sample nos. 2,3, & 4). However, there are a few peaks that are difficult to attribute to any of the three constituent salts. These new peaks are expected to be due to the formation of new phases/species, and will be investigated in more detail.

Figure 13 shows the XRD spectra of reactor feed (Sample no. 14), that involved mixing coal and eutectic salt in a ratio of 9:1 and then pyrolyzing the mixture in N₂ at a temperature 100 °C higher than the melting point of the eutectic salt. Many details of the eutectic salt shown in Figure 12 are overwhelmed by the coal spectra. However, there is a distinct broad peak in the range of 40-45 ° that is observed neither in the original eutectic salt nor in any of the three catalyst constituents. This will be studied in greater detail.

Figure 14 shows the XRD spectra of gasified char (Sample no. 15), in which most of the coal appears to have been gasified and thus interference from coal is significantly lower. When one compares Figure 12 to Figure 14, there are several new peaks present in the gasified char sample (e.g., at 22°, 34°, 63°, 75°, 79°, 95°, 111°, 119°) that were not present in the original eutectic salt or in the pyrolyzed coal feed. This aspect will be studied in more detail as it might suggest potential catalyst deactivation species that are formed during the coal gasification process. This has the potential of suggesting pathways for recovering and regenerating deactivated catalysts.

3.4 Other Accomplishments

Students Supported under this Grant included:

- Antron Palmer and Tamara Gray, both graduated with BS in chemical engineering from Clark Atlanta University (CAU) in May 1999. They are currently working with Milleken Corp. and Foster Wheeler respectively.
- Pamela Reid is a senior in chemical engineering at CAU and is due to graduate in May 2000. She plans to go to graduate school at Georgia Tech.
- Teona Edwards and Latanya Funches are juniors in chemical engineering at CAU
- Anuradha Godavarty, graduated with a Masters degree in chemical Engineering from The University of Tennessee Space Institute (UTSI) in August 1999.
- Chandramouli Sastry, joined the project team to pursue a masters degree in chemical engineering at UTSI.
- Megan Czarny and Gary Gray are undergraduate students in chemical engineering at Georgia Institute of Technology.

4 CONCLUSIONS:

The gasification experiments were carried out using two different eutectic salt mixture of $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (LNK) and $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (NK). Experiments were carried out to study a simple kinetic expression of the Langmuir-Hinshelwood type for a heterogeneous reaction. The effect of the amount of steam on the water-gas shift reaction was elucidated by the experiments carried at different steam flow rates for both catalyst systems. It was found to be in accordance to the thermodynamics of the shift reaction. A simple Langmuir-Hinshelwood model, excluding the effect of hydrogen inhibition provided a reasonably good fit to the experimental runs at different temperatures and steam flow rates.

At 10 wt % of catalyst loading, the activation energy of the ternary catalyst system (LNK) was about half (98kJ/mol) the activation energy of the single catalyst system (K_2CO_3), which is about 170 kJ/ mole. The binary catalyst system (NK) showed an activation energy of about 201 kJ/mol, which is slightly higher compared to the K_2CO_3 catalyst system.

Eutectics such as LNK system are in liquid state during gasification, i.e. the melting point of the eutectic is less than the gasification temperature. Therefore, they tend to enhance the gasification rates significantly than the eutectics which do not go into a liquid phase during the gasification process (i.e. the NK system, which is believed to be solid solution at gasification temperature). The ternary catalyst system was a much better eutectic catalyst system compared to the binary catalyst system. In general, a eutectic with a melting point less than the gasification temperature is a better substitute to the single alkali metal salts because they have a good catalyst distribution and dispersion in the carbon matrix.

The free swelling index of samples with catalyst were about 2-3 compared to 1-2 for the raw coal. The XRD characterization showed interesting spectra that require further studies before any conclusions can be drawn from the results.

The project is on schedule and continues to make good progress. The team meets regularly (every two months) to review progress.

5.0 PLANS FOR THE COMING YEAR

- Assess agglomeration tendency of catalyzed coal;
- Evaluate the recovery, regeneration and recycle of the spent catalysts;
- The bench scale fixed-bed gasification reactor studies will concentrate on the new ternary catalyst system 39% Li_2CO_3 -38.5% Na_2CO_3 -22.5% Rb_2CO_3 .
- Characterization of the catalysts, and coal/catalyst samples and products will be undertaken to access catalyst dispersion and the effectiveness of the catalysts and impregnation/addition methods.

6.0 REFERENCES

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Figure 1 Plots of fitted first order rate expression with respect to carbon for LNK catalyst system

Figure 2 Plots of fitted first order rate expression with respect to carbon for NK catalyst system

Figure 3 Possible effects of thermal gasification and system transient in the catalytic steam gasification run

Figure 4 Determination of k_1 and k_2 for the LNK catalyst system

Figure 5 Determination of k_1 and k_2 for the NK catalyst system

Figure 6 Arrhenius plots for LNK catalyst system

Figure 7 Arrhenius plots for NK catalyst system

Figure 8 Comparison of the specific gasification rates calculated from the model with the experimental results for LNK system

Figure 9 Comparison of the specific gasification rates calculated from the model with the experimental results for NK system

Courtesy of British Standards Institution

Figure 10 Full Scale Standard Profiles and Corresponding index Numbers

Figure 11. X-ray Diffraction Pattern for Fresh Coal (Sample 1)

Figure 12. X-ray Diffraction Pattern for Eutectic Salt (Sample 12)

Figure 13. X-ray Diffraction Pattern for Reactor Feed (Sample 14)

Figure 14. X-ray Diffraction Pattern for Gasified Char (Sample 15)