

CATALYTIC GASIFICATION OF COAL USING EUTECTIC SALT MIXTURES

Report for the period
September 1, 1998 to March 31, 1999

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ABSTRACT

The project, Catalytic Gasification of Coal Using Eutectic Salt Mixtures, is being conducted jointly by Clark Atlanta University (CAU), the University of Tennessee Space Institute (UTSI) and the Georgia Institute of Technology (GT). The aims of the project are to: identify appropriate eutectic salt mixture catalysts for the gasification of Illinois #6 coal; evaluate various impregnation or catalyst addition methods to improve catalyst dispersion; evaluate effects of major process variables (e.g., temperature, system pressure, etc.) on coal gasification; evaluate the recovery, regeneration and recycle of the spent catalysts in a bench-scale fixed bed reactor; and conduct thorough analysis and modeling of the gasification process to provide a better understanding of the fundamental mechanisms and kinetics of the process. During this period, the eutectic systems evaluated included: $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$, $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Rb}_2\text{CO}_3$, $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-Rb}_2\text{CO}_3$, and $\text{CaSO}_4\text{-BaSO}_4\text{-Li}_2\text{SO}_4$.

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 incipient wetness method gave more uniform catalyst distribution than that of physical mixing for the soluble catalysts resulting in higher gasification rates for the incipient wetness samples. The catalytic activity increased by varying degrees with catalyst loading. The above results are especially important since the eutectic catalysts (with low melting points) yield significant gasification rates even at low temperatures. Among the ternary eutectic catalysts studied, the system 39% $\text{Li}_2\text{CO}_3\text{-38.5% Na}_2\text{CO}_3\text{-22.5% Rb}_2\text{CO}_3$ showed the best activity and will be used for further bench scale fixed-bed gasification reactor in the next period.

Based on the Clark Atlanta University studies in the previous reporting period, the project team selected the 43.5% $\text{Li}_2\text{CO}_3\text{-31.5% Na}_2\text{CO}_3\text{-25% K}_2\text{CO}_3$ ternary eutectic and the 29% $\text{Na}_2\text{CO}_3\text{-71% K}_2\text{CO}_3$ binary eutectic for the fixed-bed studies at UTSI during this reporting period. Temperature was found to have a significant effect on the rate of gasification of coal. The rate of gasification increased up to 1400 °F. Pressure did not have much effect on the gasification rates. The catalyst loading increased the gasification rate and approached complete conversion when 10 wt% of catalyst was added to the coal. Upon further increasing the catalyst amount to 20-wt% and above, there was no significant rise in gasification rate. The rate of gasification was lower for a 2:1 steam to char molar ratio (60%) compared to gasification rates at 3.4:1 molar ratio of steam-to-char where the conversion approached 100%. The characterization results of Georgia Tech are very preliminary and inconclusive and will be made available in the next report.

The project is on schedule and continues to make good progress. The project team meets regularly (at least every two months) to review the progress 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 September 1998 to March, 1998. 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 task is given in the next section.

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 (hvCb 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 . 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 $100\text{ }^\circ\text{C}$ above the respective eutectic melting points. After cooling, the solidified melts were crushed and finely ground in an agate mortar.

B Preparation of samples (coal + catalyst):

B-1 Physical mixing technique

Salt mixtures at their eutectic composition or eutectic catalysts were finely ground in an agate mortar and weighed amounts were then intimately mixed with the powdered coal in a Fisher Minimill to give an initial catalyst concentration of 10 wt % of each catalyst.

B-2 Incipient wetness method

Weighed powdered salt mixtures or powdered eutectic catalysts were added to the powdered coal and shaken for two hours. Water was then added to the coal catalyst mixture. The sample was subsequently dried in air for three days. Based on preliminary studies on the amount of water absorbed or needed to completely cover a given amount of coal, the ratio of water to coal was kept at 0.62 ml of water/gram of coal in the experiments.

C Gasification Test by TGA

In order to compare the relative catalytic effects of the different catalysts in the gasification of coal with carbon dioxide, mixtures of powdered coal with 10 wt % of the different catalysts were prepared by two methods and the rate of weight loss of the samples when heated in a flowing gas of CO_2 were measured at a series of constant temperatures. The catalyst samples studied during this period are summarized in Table 2.

Measurements of gasification kinetics in flowing CO_2 [140 ml/min at 1 atm (0.1MPa)] were performed in a SDT 2960 Simultaneous DTA-TGA. Simultaneous thermal gravimetry-differential thermal analyses (TG-DTA) were performed at a linearly increasing temperature rate of $dT/dt = 10\text{ }^\circ\text{C}/\text{min}$ in an atmosphere of flowing carbon dioxide gas. The balance was usually operated in the isothermal mode with weight changes being recorded as a function of time and temperature at a series of TGA settings in the range $450\text{-}1000\text{ }^\circ\text{C}$. At each temperature, gasification was continued for ~ 10 min to assure that steady state conditions were attained. The gasification rate at each temperature and time were derived from the relation:

$$\text{rate (min}^{-1}\text{)} = -(\text{dW}/\text{dt}) \cdot (1/\text{W})$$

where W is the weight of the sample at time t.

2.2 Task 2: Evaluation of gasification performance in bench-scale fixed-bed reactor

The high-pressure, high-temperature fixed-bed catalytic coal gasification experiments using eutectic salt mixtures were carried out at UTSI to initially choose a better catalyzed coal preparation technique and to optimize the process variables for an efficient gasification process.

A Sample preparation

The ternary and binary catalysts were added to raw coal by physical mixing and pyrolyzed at 750 °C for 3 hours. The pyrolyzed char was crushed and sieved to get a feed to the reactor whose particle size varied between 30 mesh and 100 mesh. The char was gasified at various conditions of temperature, pressure, catalyst weight percent, and molar ratio of steam to char.

B Catalyst Addition Techniques

The techniques that were used during the course of experimentation at UTSI included:

B-1 Physical Mixing (M1)

The alkali and alkaline earth metal salts were used as a catalyst mixture at its eutectic composition. This mixture was heated to about 100 °C above its melting point to form a eutectic. The resulting glassy material was then crushed and added to coal in required amounts.

B-2 Wet Mixing of Eutectic Salts (M2)

The eutectic mixture prepared by the above method was made into a slurry (because it was insoluble in water) by adding sufficient amount of water to just wet the coal (i. e. incipient wetness method). The thick paste was thoroughly mixed for good distribution of the catalyst and then dried in an oven at ~110 °C for 12 hours. The resulting dry coal was crushed in an agate mortar and subsequently used for pyrolysis in a tube furnace.

C Devolatilization/Pyrolysis

The devolatilization step was carried out separately from the gasification step to avoid the difficulties in handling the tars that come out during pyrolysis. The dry crushed coal with catalyst was filled in small sample boats and, placed in the stainless steel reactor to be heated in the tubular furnace – Mellen Model TS-2200-231-3. Pyrolysis was carried at 1350 °F for 3-4 hours under N₂ atmosphere. The pyrolyzed coal was cooled under inert conditions, crushed using agate mortar and sieved to collect fractions between 30 mesh and 100 mesh. This fraction was used for gasification.

D 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 its 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.

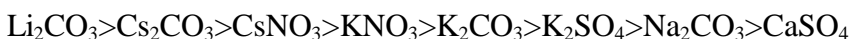
The conversions based on TGA results were calculated using the formula below:

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

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

3 SUMMARY OF RESULTS AND DISCUSSION

In our previous report, the results for several single salt catalysts and binary and ternary eutectic catalysts investigated at Clark Atlanta University were presented (2,3). Physical mixing and incipient wetness method were investigated as catalyst addition techniques. Gasification was carried out using TGA and a fixed-bed reactor. The results showed better gasification activity in the presence of the catalysts tested. The order of catalytic activity of eight single salt catalyst tested was:



The eutectic salt studies showed clear agreement between the melting points of the prepared eutectic and reported literature values. The order of catalytic activity observed was ternary > binary > single. The incipient wetness method was found to give better results than physical mixing technique. Also, catalyst preparation conditions such as catalyst loading, drying time and temperature were found to influence the gasification rate (3).

3.1 Evaluation of the eutectic catalysts and application methods

The results of the kinetic experiments with the samples from Tables 2 are shown in Figures 1-2. These results were obtained by the physical mixing technique. The gasification rates of the coal with catalysts were greater than that with the raw coal.

Table 2 Ternary eutectic mixtures studied

No	Eutectic Salt Mixtures (Mol %)	M.P. (°C)
1	43.5%Li ₂ CO ₃ -31.5%Na ₂ CO ₃ -25%K ₂ CO ₃	400
2	49.5%Li ₂ CO ₃ -44.5%Na ₂ CO ₃ -6%K ₂ CO ₃	468
3	39%Li ₂ CO ₃ -27.9%Na ₂ CO ₃ -33.1%K ₂ CO ₃	349
4	58%Na ₂ CO ₃ -3%K ₂ CO ₃ -39%Rb ₂ CO ₃	558
5	22%Li ₂ CO ₃ -38%Na ₂ CO ₃ -40%Rb ₂ CO ₃	410
6	39%Li ₂ CO ₃ -38.5%Na ₂ CO ₃ -22.5%Rb ₂ CO ₃	400
7	50%Li ₂ CO ₃ -29%Na ₂ CO ₃ -21%Rb ₂ CO ₃	412
8	14%CaSO ₄ -6%BaSO ₄ -80%Li ₂ SO ₄	660

For the incipient wetness method samples, similar results were obtained as in Figure 3. Compared to the results for the same composition samples prepared by physical mixing, the incipient wetness method showed more significant gasification at the same temperature (Figures 4-5). The incipient wetness method probably increases the catalyst dispersion and offers more effective active sites, thereby resulting in a higher gasification rate.

With ternary eutectic catalysts added to the coal, marked increases in gasification rates were observed (see Figures 1-5). The low melting eutectics were found to be very active. It is very interesting to compare the differences in catalyst activity for the same composition samples prepared by different application methods. The results follow the same trend. Thus, the incipient wetness method yielded higher results than the physical mixing technique. It is possible that the physical state of the catalyst may influence the relative catalytic activity. The observed activity order of incipient wetness>physical mixing, may be ascribed to dispersion effects. The incipient wetness method allows the catalyst to penetrate into the pores of the coal sample and also enhances uniform distribution of the catalyst within the coal thereby increasing the dispersion, catalyst utilization and effectiveness. Comparing the activities of the above catalysts, 39%Li₂CO₃-38.5%Na₂CO₃-22.5% Rb₂CO₃ showed the best activity and will be used for further study in the bench scale fixed bed reactor in the next period.

3.2 Fixed Bed Gasification Results

Based on the Clark Atlanta University studies during the previous period, the project team selected the 43.5%Li₂CO₃-31.5%Na₂CO₃-25%K₂CO₃(LNK) ternary eutectic and the 29%Na₂CO₃-71%K₂CO₃ (NK) binary eutectic for the fixed bed studies at UTSI. The effects of major process variables such as temperature, system pressure and molar ratio of steam to char on coal gasification were evaluated.

Temperature was found to have a significant effect on the rate of gasification of coal using LNK as catalyst (Figures 6-6a). The rate of gasification increased up to about 1400 °F, and then leveled off. The pressure did not have much effect on the gasification rates (see Figures 7-7a). The amount of catalyst increased the gasification rate and approached complete conversion when 10 wt % of catalyst was added to the coal compared to only around 60% conversion for a 5 wt % addition of LNK. Upon further increasing the catalyst amount to 15%, there was an insignificant rise in gasification rates (Figures 8-8a). The catalytic gasification of coal using LNK as catalyst under steam with a 2:1 molar ratio did not give complete conversion (X_c=60%)(Figures 9-9a). The rate of gasification for the 2:1 molar ratio was low compared to gasification rates at 3.4:1 molar ratio of steam-to-char where conversions approached 100%. On further increasing the ratio to 5.5: 1, a very slight increase in specific gasification rates was obtained compared to the 3.4 : 1 steam to char ratio data.

In Figure 10, the gasification of the catalytic reaction was found to increase with the temperature at which the reaction was carried out. At 1420 °F, the conversion was almost complete. The binary Na₂CO₃-K₂CO₃ (NK) catalyst was added to the raw coal by two different techniques (see Figure 11). The first method was by physical mixing of the catalyst to the raw coal. It was then pyrolyzed and gasified at chosen conditions of temperature, pressure, catalyst loading and steam to char ratio. In the second method, a catalyst solution was added to the raw coal and then dried at 110 °C for 12 hours. It was then pyrolyzed and gasified under the chosen standard conditions. It was observed that the rate of gasification was higher for physical mixing technique than the solution method. In comparison to LNK catalyst being added to the raw coal by the solution technique, the NK catalyst gave a higher gasification rate of the reaction by the same method of catalyst application. This could possible be due to the solubility of the NK catalyst in water, as compared to the LNK catalyst which is insoluble in water (Figures 11a-11b).

3.3 Characterization

The characterization results initiated at Georgia Tech during this period were very preliminary and inconclusive and will be presented in the next report.

4 CONCLUSIONS:

The eutectic catalysts increased gasification rate significantly. The methods of catalyst preparation and addition have significant effect on the catalytic activity and coal gasification. The incipient wetness method gave more uniform catalyst distribution than that of physical mixing for the soluble catalysts resulting in higher gasification rates for the incipient wetness samples. The catalytic activity increased by varying degrees with catalyst loading. The above results are especially important since the eutectic catalysts (with low melting points) yield significant gasification rates even at low temperatures.

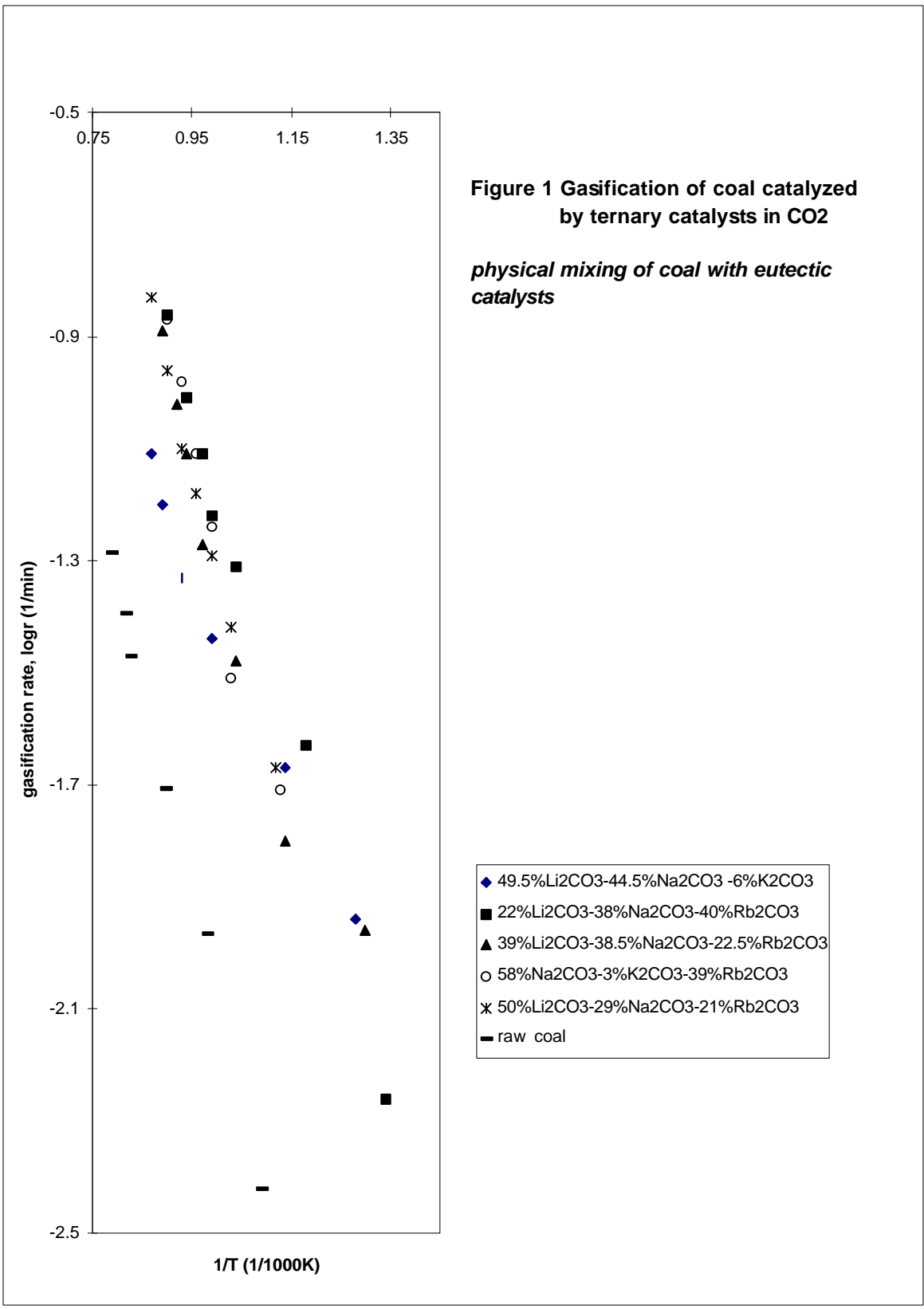
Temperature was found to have a significant effect on the rate of gasification of coal. The rate of gasification increased up to 1400 °F. Pressure did not have much effect on the gasification rates. The amount of catalyst increased the gasification rate and approached complete conversion when 10 wt % of catalyst was added to coal. The rate of gasification was lower for a 2:1 steam to char molar ratio compared to gasification rates at 3.4:1 molar ratio of steam-to-char where the conversion approached 100%.

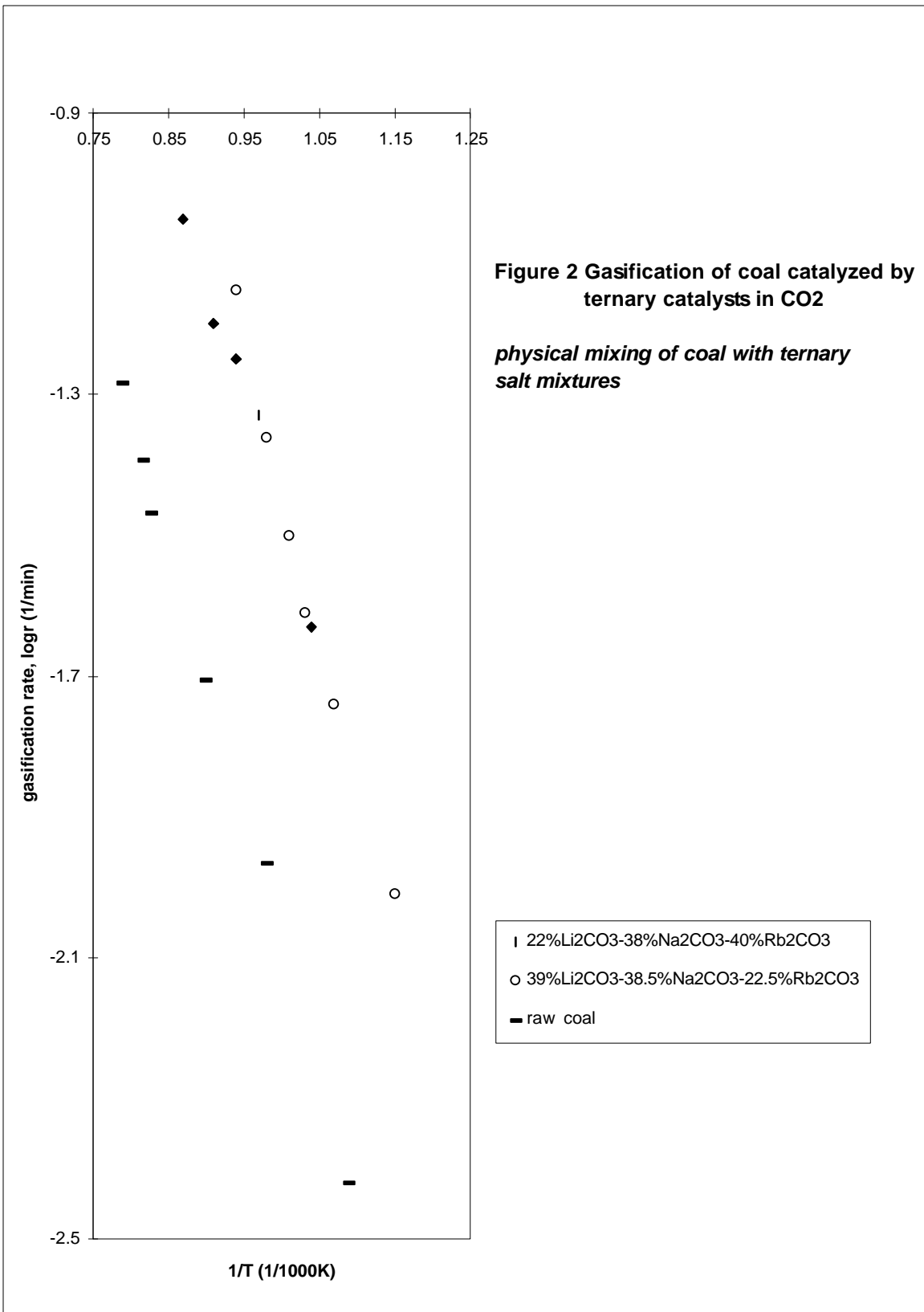
PLANS FOR THE COMING YEAR

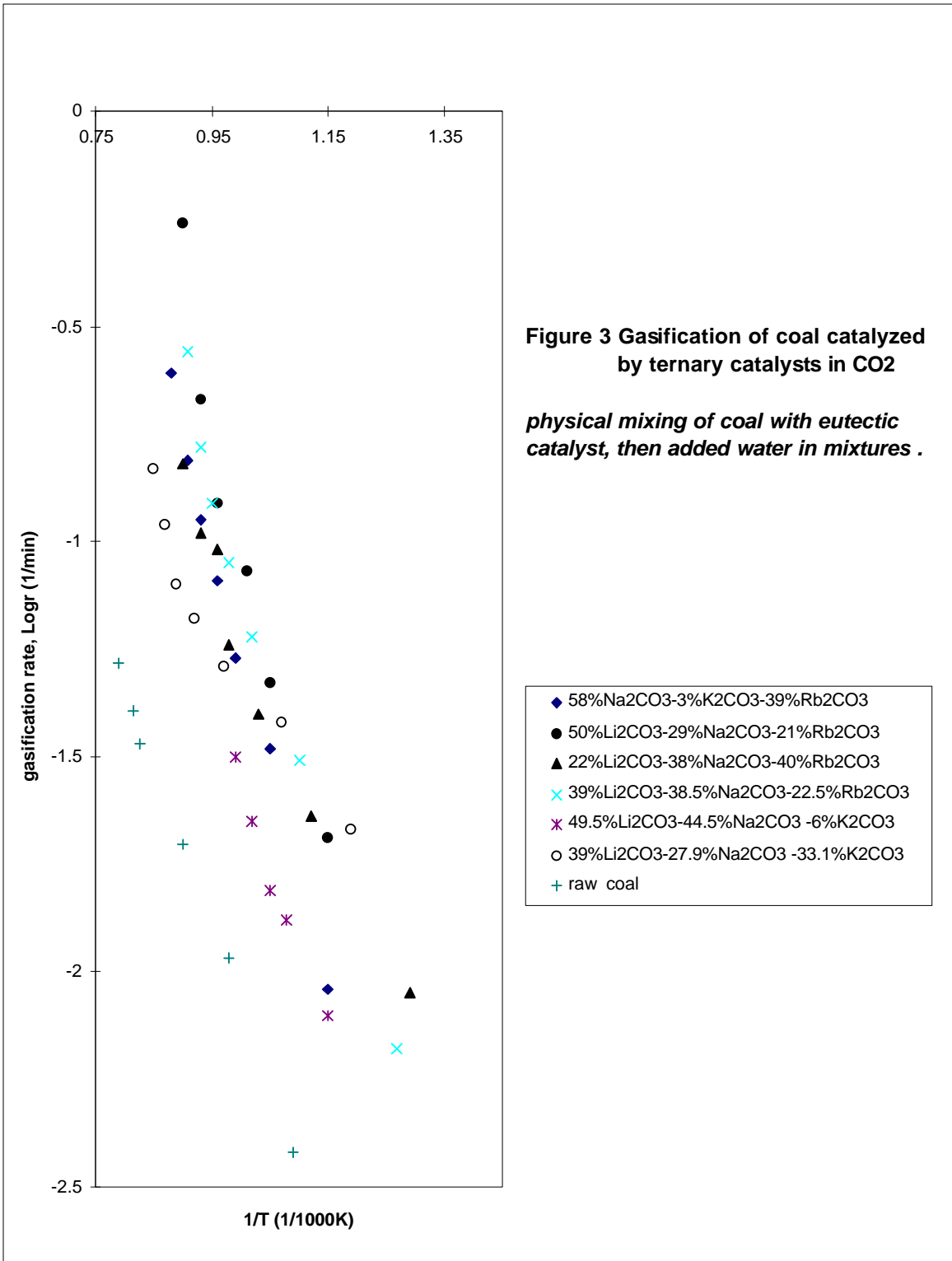
- Assess agglomeration tendency of catalyzed coal;
- Evaluate the recovery, regeneration and recycle of the spent catalysts;
- Initiate analysis and modeling of the gasification process to provide better understanding of the fundamental mechanisms and kinetics of the process;
- The bench scale fixed-bed 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 assess catalyst dispersion and the effectiveness of the catalysts and impregnation/addition methods.

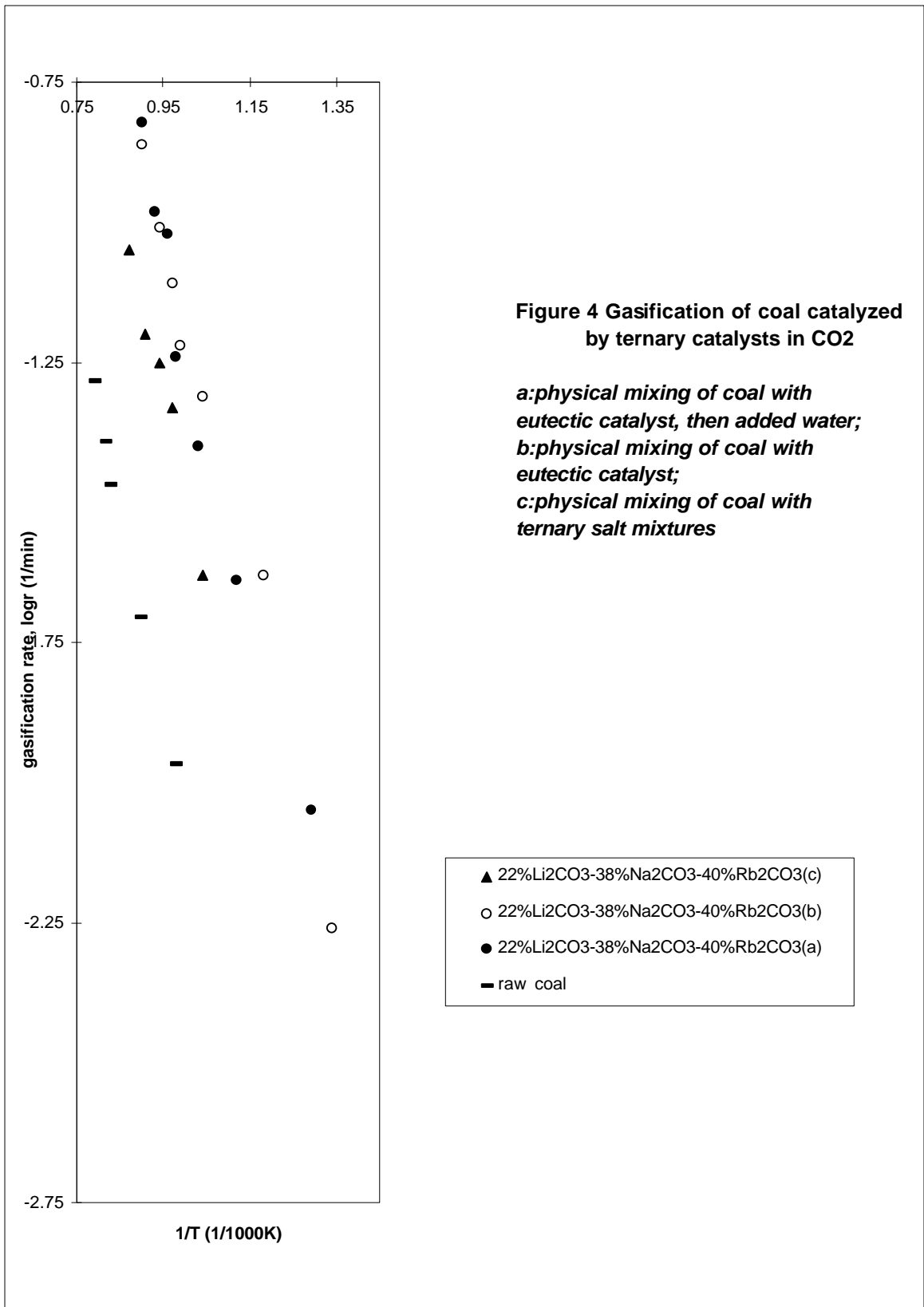
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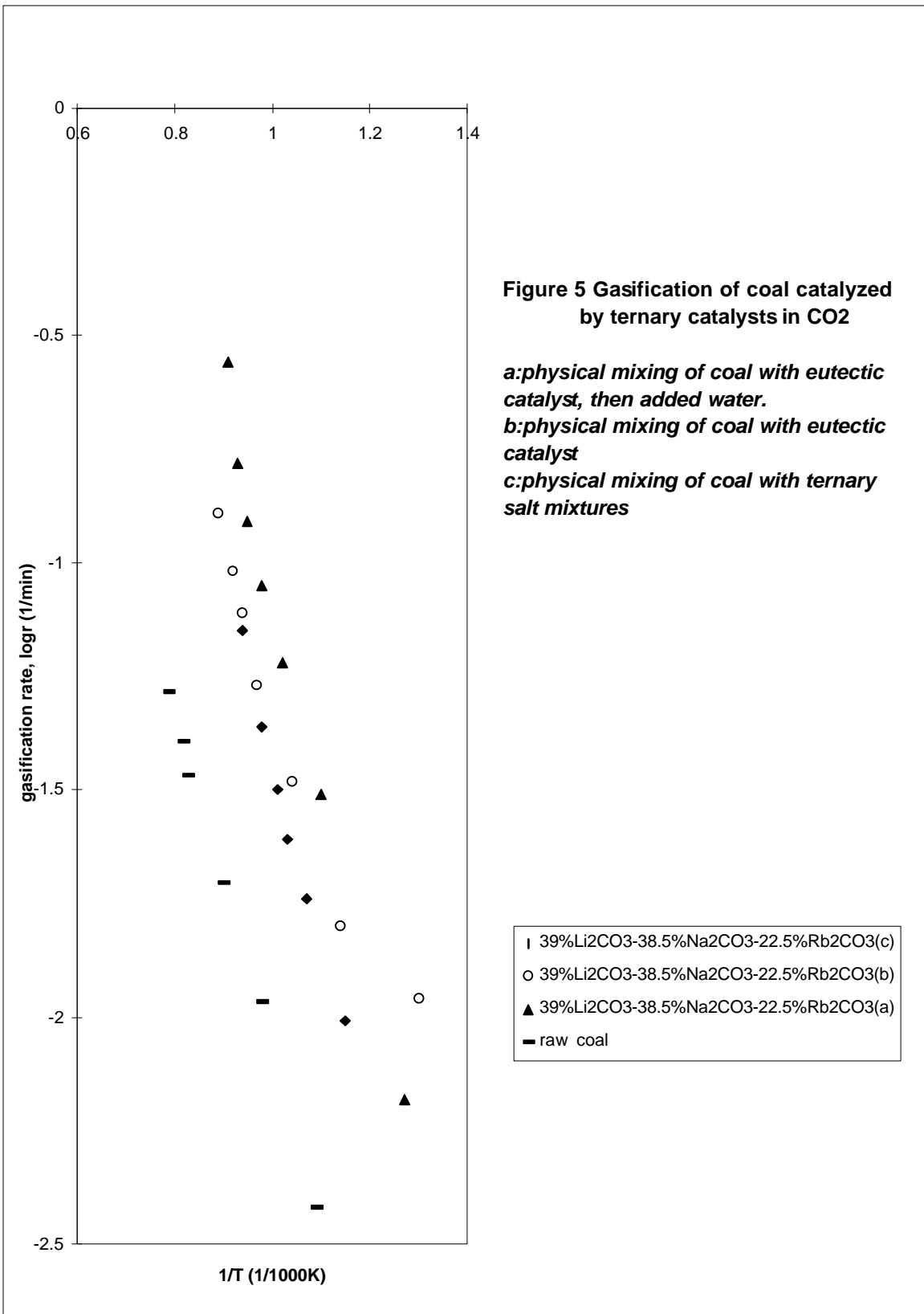


Figure 6 The effect of temperature on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

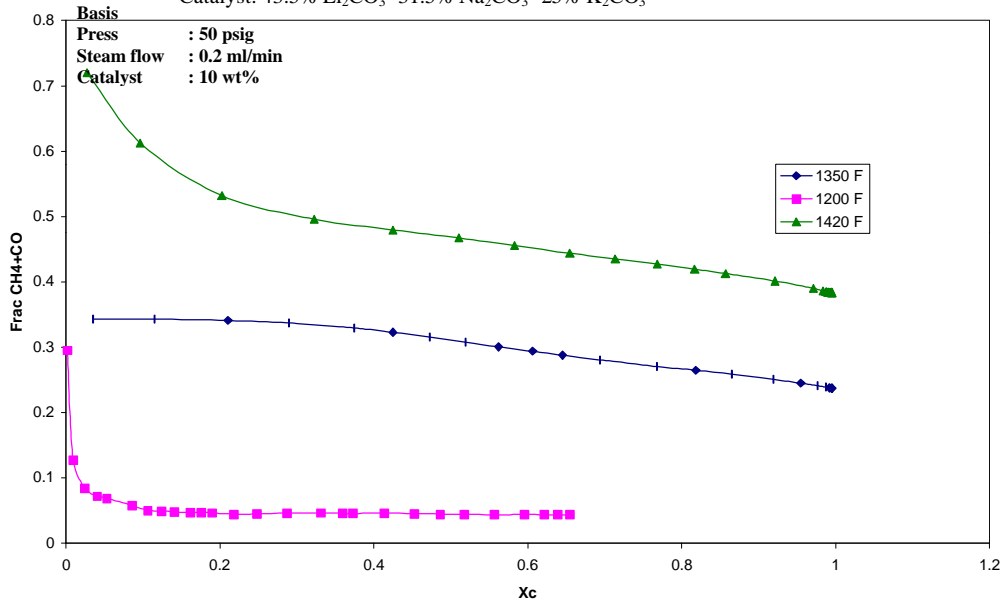


Figure 6a The effect of temperature on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

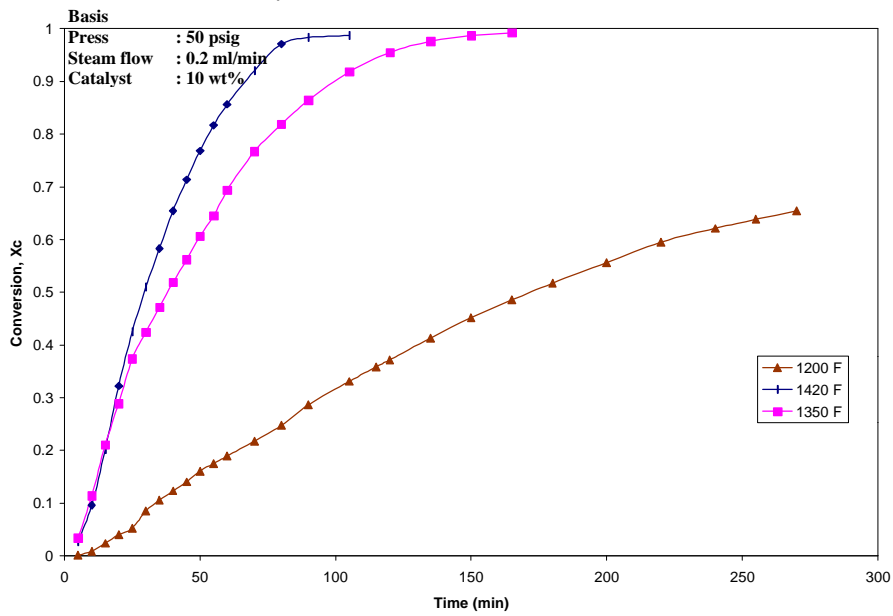


Figure 7 The effect of pressure on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

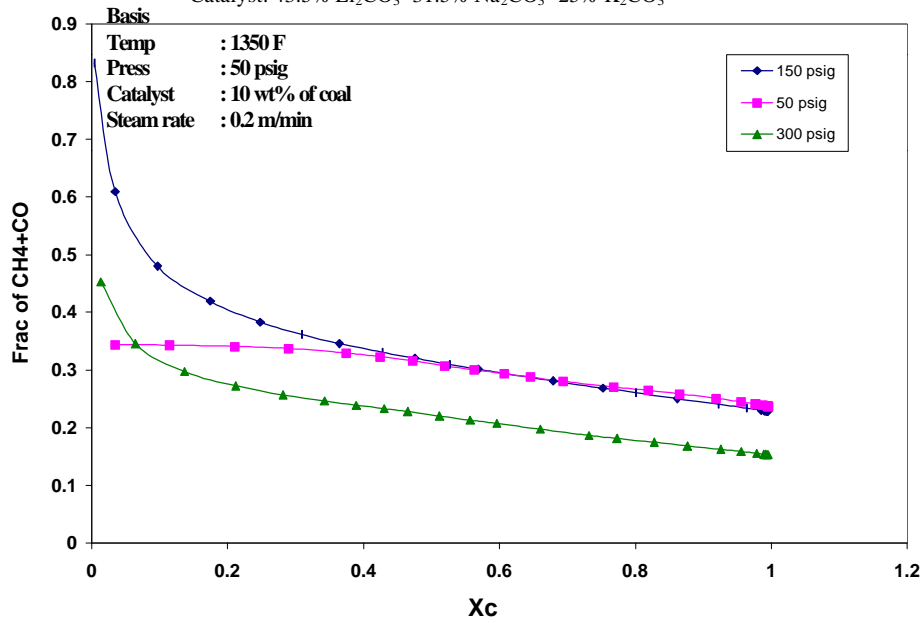


Figure 7a The effect of pressure on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

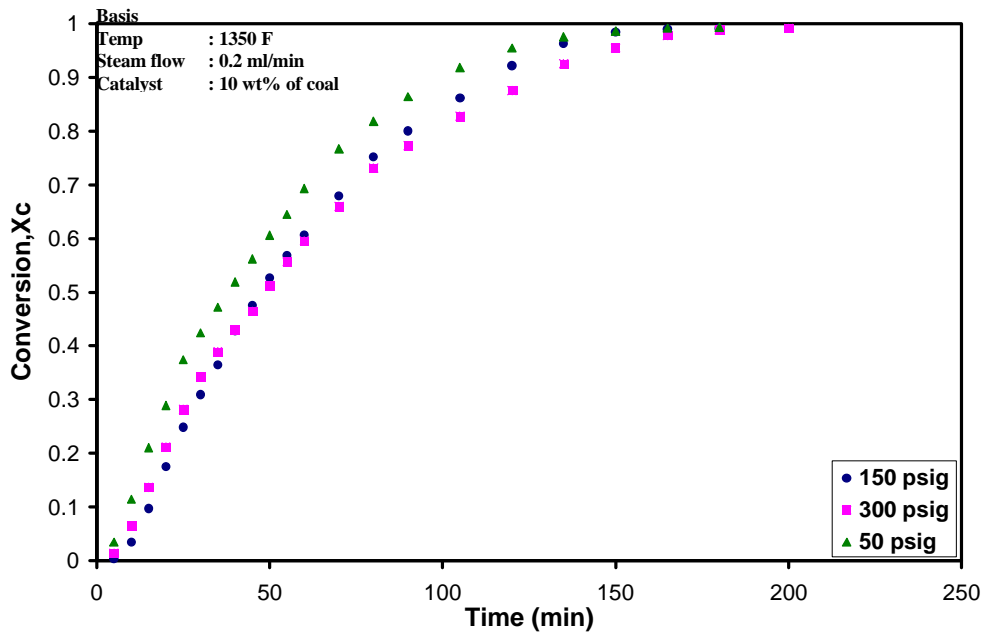


Figure 8 The effect of catalyst loading on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

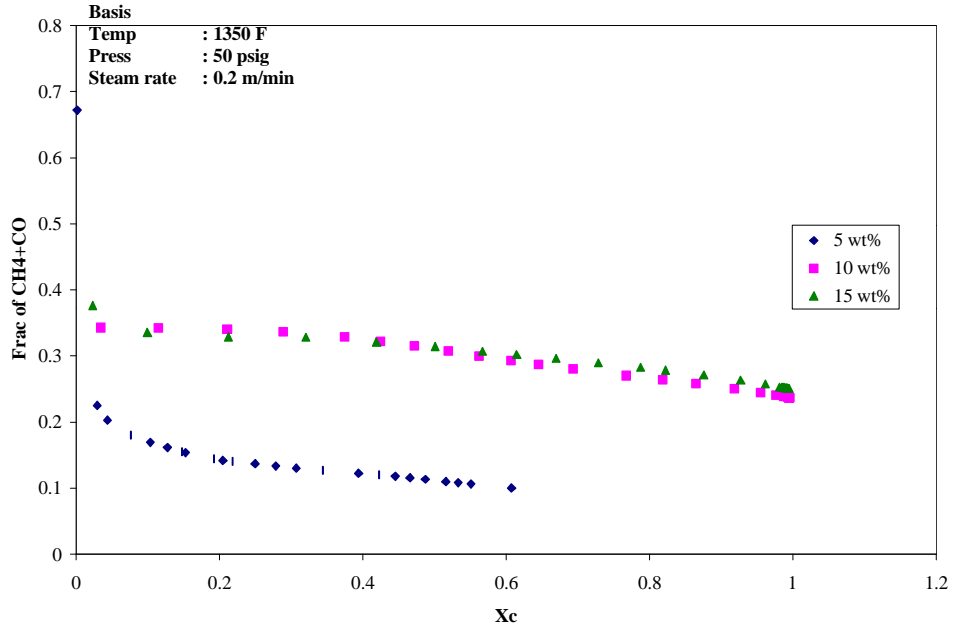


Figure 8a The effect of catalyst loading on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

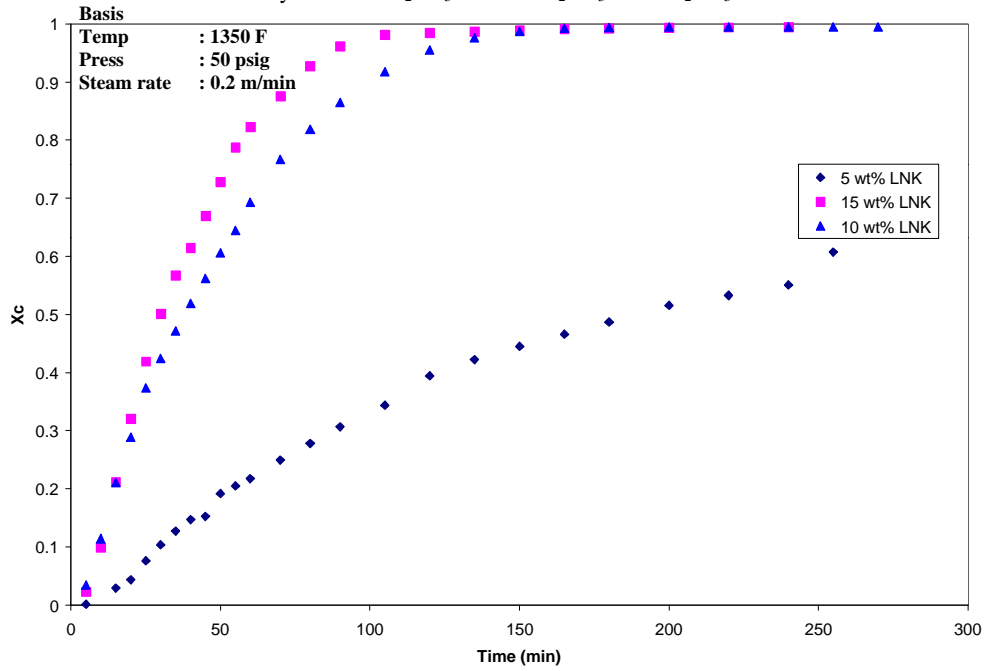


Figure 9 The effect of molar ratio of steam to char on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

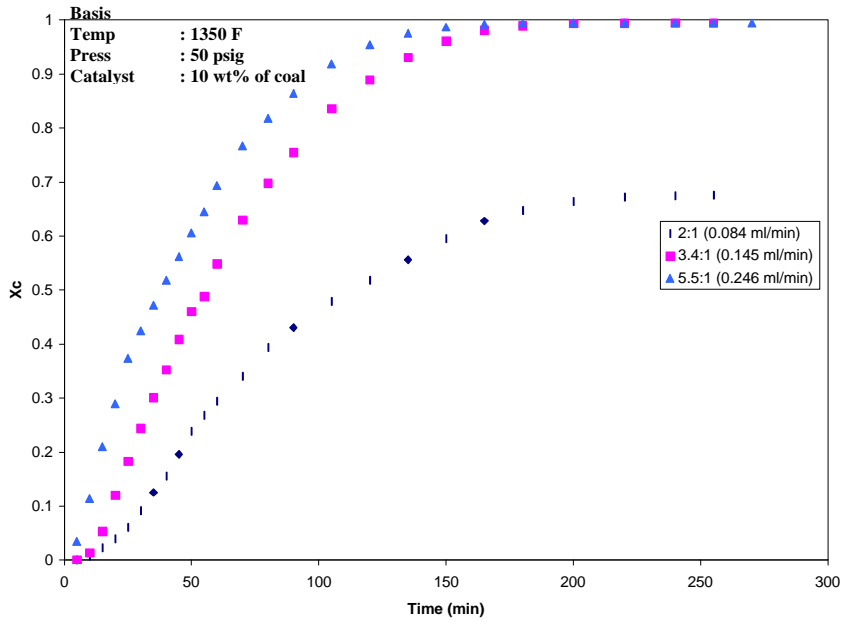


Figure 9a The effect of molar ratio of steam to char on the gasification
 Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

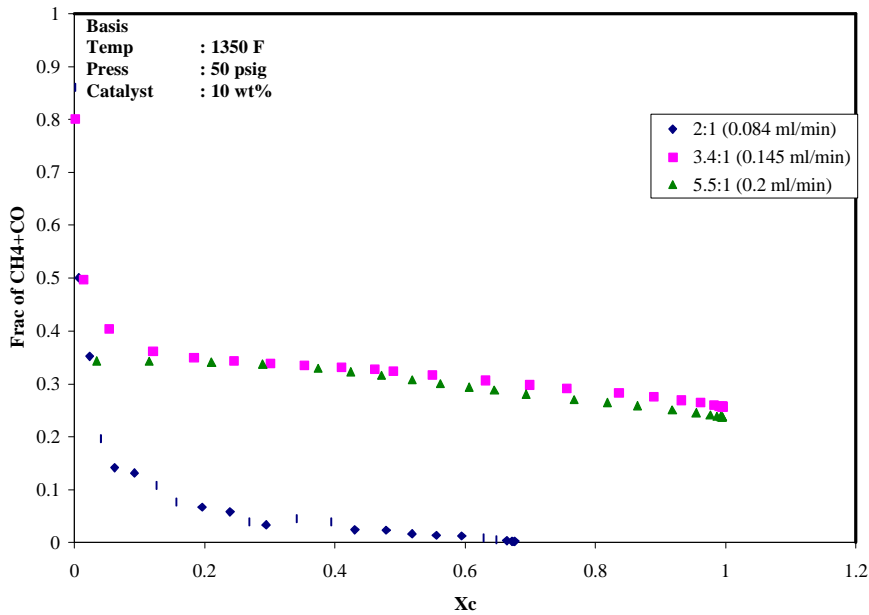


Figure 10 The effect of temperature on the gasification
 Catalyst: 29% Na₂CO₃- 79% K₂CO₃

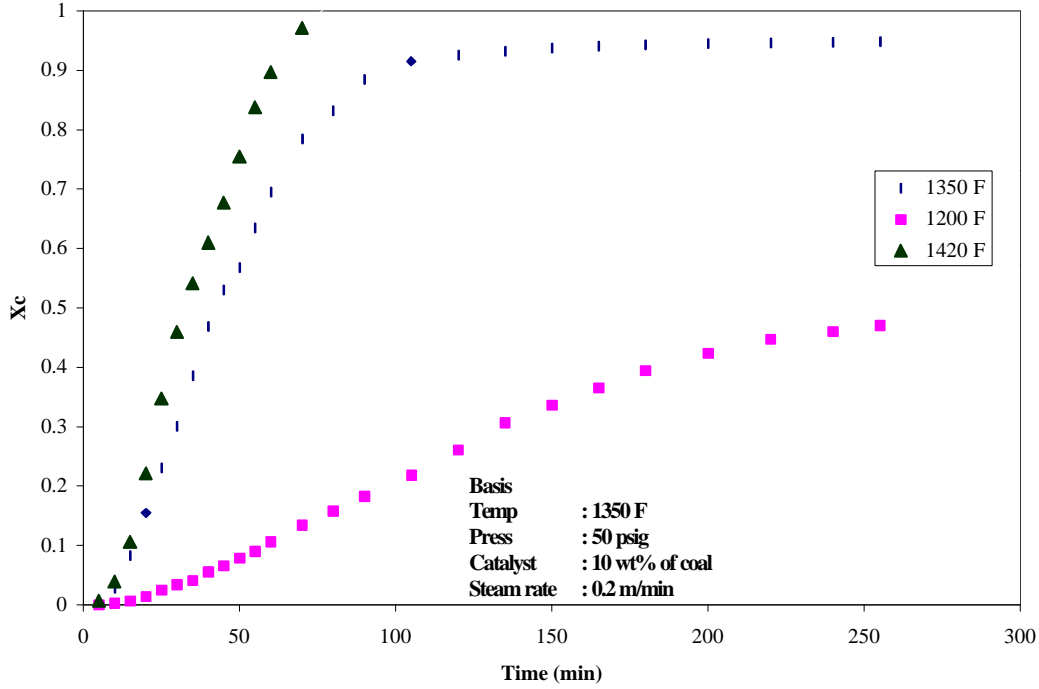


Figure 11 The effect of catalyst application technique on the gasification
 Catalyst: 29% Na₂CO₃- 79% K₂CO₃

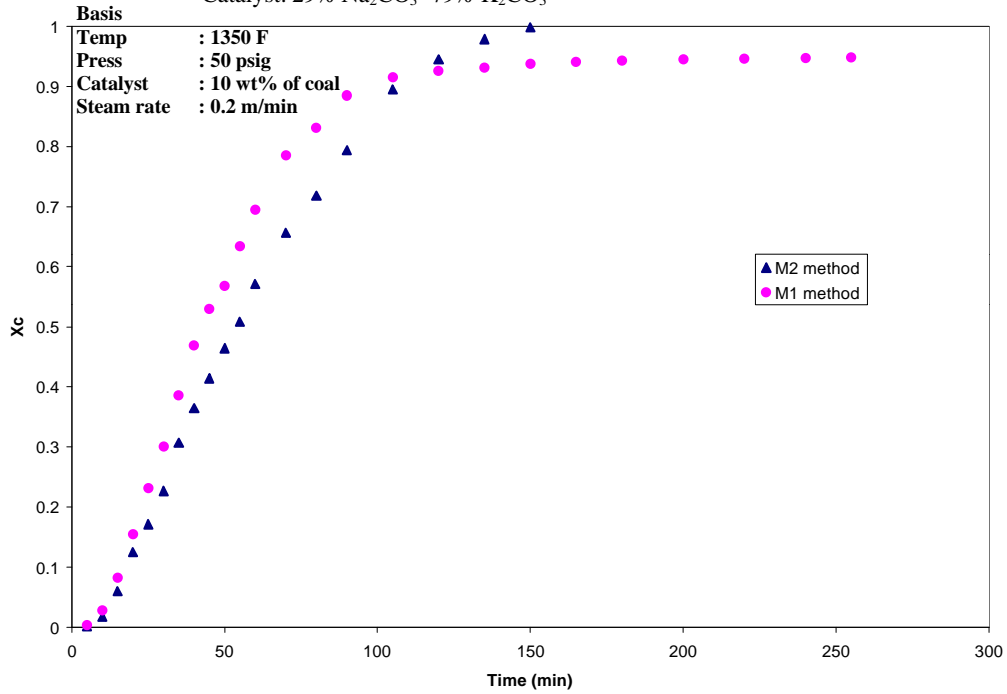


Figure 11a The effect of catalyst application technique on the gasification

Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

29% Na_2CO_3 - 79% K_2CO_3

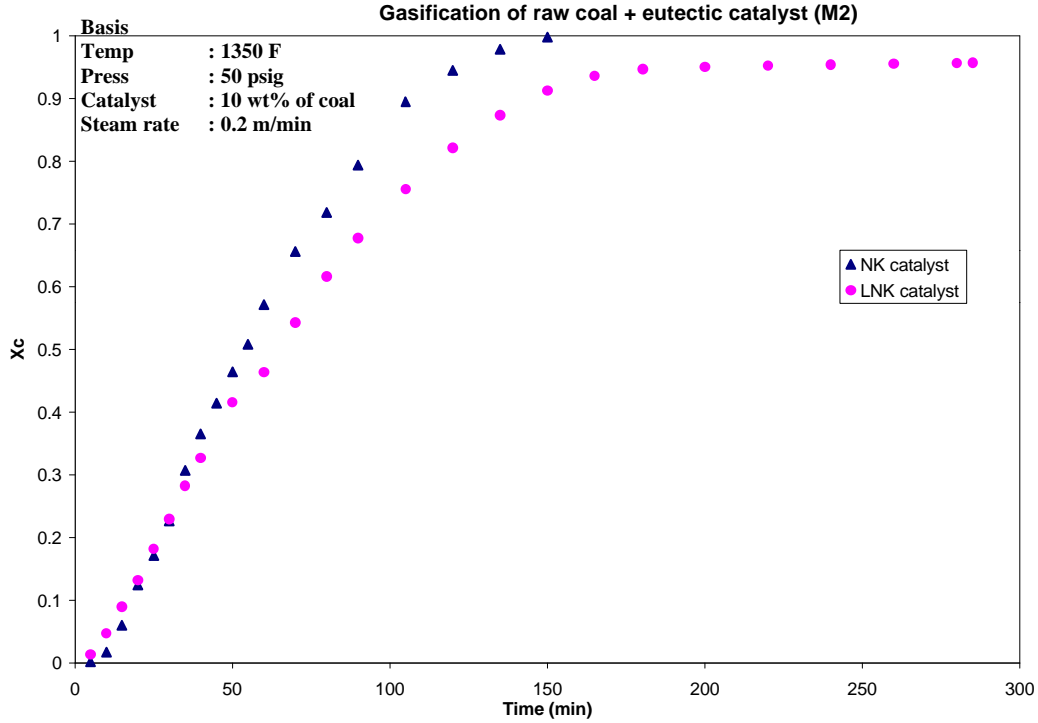


Figure 11b The effect of catalyst application technique on the gasification

Catalyst: 43.5% Li_2CO_3 - 31.5% Na_2CO_3 - 25% K_2CO_3

29% Na_2CO_3 - 79% K_2CO_3

