

Hydrogen from Coal Using Reaction Swing Approach

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EXTENDED ABSTRACT

An innovative scheme to separate hydrogen from coal gasification products for end users such as clean energy production is presented. The main approach of this process is the use of catalysts (Me) in a fixed bed reactor that will increase hydrogen purity by CO disproportionation that yields in elemental carbon and carbon dioxide. The resulting carbon dioxide immediately reacts with specially modified calcium based component that acts as a carbon dioxide removal material (CDRM), thus producing carbon-based-gases-free hydrogen. The reverse flow of air is used to regenerate the carbon-loaded catalyst and the heat liberated via the exothermic reaction is utilized to regenerate carbon dioxide capture agent releasing carbon dioxide. Thus, the product of this system would result into hydrogen ready for use in fuel cells. Figure 1 shows the schematic of the process.

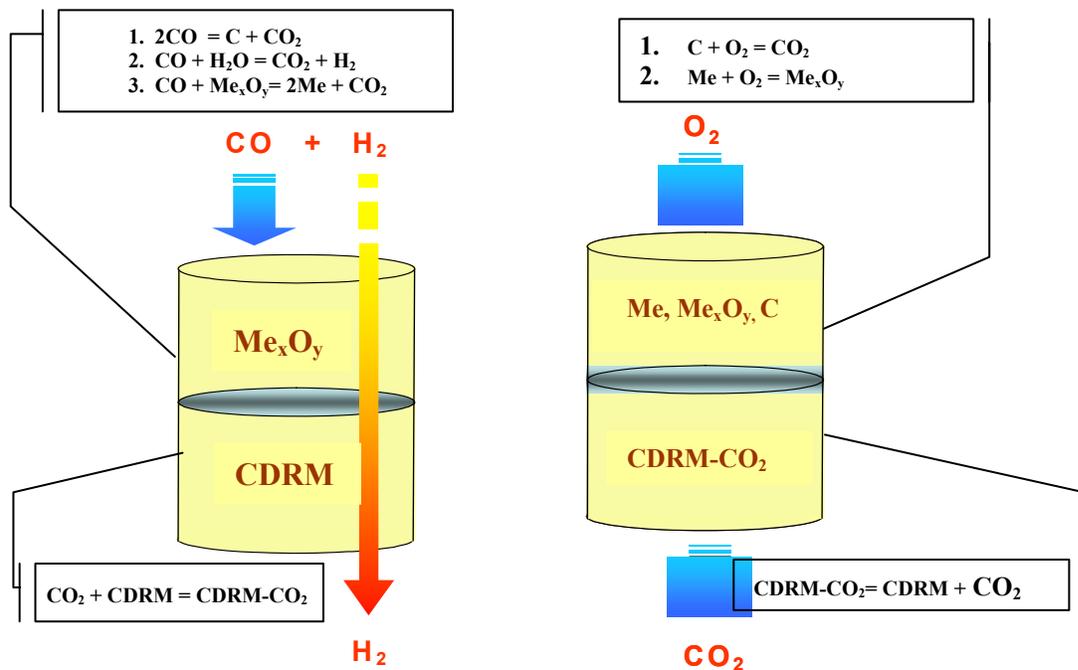


Figure 1 (a) Hydrogen Enrichment (b) Regeneration of catalyst and CDRM
Schematic of the proposed process

Pure hydrogen stream was produced from different syngas mixtures. The effect of the process parameters such as temperature, steam content, syngas composition, syngas content in the feed stream, residence time etc., on conversion efficiency are presented. The response variables used for determining the optimal catalyst preparation conditions were the reactivity and extent with respect to CO disproportionation, hydrogen purity, catalyst deactivation, and will be related to the porosity, pore radii, dispersion on the support, and particle size. Experiments were also conducted to evaluate the effect of solids composition on the product gases. In the absence of any steam, some degree of methane formation was observed when the gas flow rate was high/short contact time. No significant loss in hydrogen yield was observed even when no steam was added.

EXPERIMENTAL PROCEDURE

The small scale laboratory reactor was set up for those experiments. The reactor system consist of gas supplies, water pump, steam generator, reactor system (reactor + furnace), water trap and gas collection system and the required fitting and flow measurement devices. The catalyst and the CDRM was placed sequentially in the reactor and the reactor was heated to the predetermined temperature under nitrogen flow. In the experiments with coal, the empty furnace was heated to the predetermined temperature while the reactor (with catalyst, CDRM and coal) was flushed with nitrogen at room temperature. Upon reaching the temperature, the reactor was inserted to the high temperature region. Once the predetermined temperature was achieved, nitrogen flow was reduced and the gas flow was compensated with a predetermined amount of steam and syngas. The product gases were passed through a microGC 3000 from Agilent Technologies to provide real-time data analysis. The microGC consists of two separate channels, one with Plot Q column and other with Molecular Sieve 5A column and 2 TCDs. It is capable of analyzing samples containing CO, H₂, CO₂, CH₄, C₂H₆, O₂ and N₂ in less than 2 minutes. Figure 2 is a schematic of the setup. Syngas cylinders containing 20, 43 and 48 % H₂ (with the balance CO) were obtained from syngas. Experiments were conducted to establish baselines such as residence time distributions for each gas at different flow rates and temperatures. Experiments with syngas were conducted to study the effect of gas flow rates (25 – 100 ml/min), syngas content (from 5 to 50 %), temperature (650 -850 °C), steam, syngas composition, solids loading (Fe₂O₃ loadings of 0.14 – 2 g and CaO loadings of 0.56 – 6 g) and solids ratio on the hydrogen purity and cycle time for enrichment.

RESULTS AND DISCUSSION

HYDROGEN ENRICHMENT FROM SYNGAS

Table 1 shows the effect of temperature on the hydrogen enrichment and solids regeneration. It can be clearly seen there that hydrogen enrichment goes through a maxima around 800 °C, however due to the intensive CO₂ removal the lowest gas yield was observed at that temperature.

The evaluation of the key process parameters revealed that the actual moles of syngas flowing and the amount of the active solids are the most significant factors. It was thus observed that a high residence time and high syngas content or a low residence time and low syngas content provide the optimal enrichment cycle time. A set of experiments were conducted at different catalyst to calcium oxide ratios, ranging from 1:1 to 1:36. Figures 3 and 4 contain the plots of the gas content as a function of time for the cases of Me_xO_y:CDRM ratios of 1:12 and 1:36. The hydrogen content increased from the feed content of 48 % to nearly 80

% in both cases. The addition of steam under these conditions resulted in greater than 95 % H₂ in the product gas stream for the former case while it was nearly 100 % for the latter case. Some amount of methane was observed in the absence of steam in both cases. This was found to be the result of methanation of the carbon deposited from the Boudouard reaction with the excess hydrogen.

Table 1. Data on Experiments using Me_xO_y (0.5g) and CDRM (0.5g)

		H ₂ %	CO %			
Inlet		48	52			
		Enrichment			Regeneration	
Temp	Gas Yield	H ₂	H ₂ Recovery	C removed	CO ₂ from C	CO ₂ in CaCO ₃
°C	%	%	%	%	%	%
750	78	60	80	82	-	-
800	48	98	95	92	35	65
850	68	72	100	54	20	80

Figures 5 a, and b and Figure 6 a and b show the effect of syngas content on the outlet gas composition. All the experiments were conducted with a catalyst:CDRM ratio of 1:3 at 750 °C. Figure 5 a contains the data on the experiments conducted with 20% syngas in N₂ while Figure 5 b contains the data for the experiments conducted with 50 % syngas mixture in N₂. Figure 6 a and b are the outlet gas compositions of the experiments conducted at higher flow rates for feed syngas contents of 20 and 50 %, respectively. It is seen that increasing the flow rate (for a given syngas content) shortens the cycling time significantly.

SIMULTANEOUS COAL GASIFICATION AND HYDROGEN ENRICHMENT

Simultaneous coal gasification and hydrogen enrichment experiments were conducted. We already have experience with the gasification of several coal samples. However, a few initial runs of coal gasification alone were conducted to establish the gas composition from gasification. The effect of temperature, steam partial pressure, and coal loading on the conversion degree and hydrogen yield was evaluated. Following this the simultaneous gasification-enrichment processes were conducted. In this set, the reactor containing the catalyst and CDRM was introduced into the reactor. Nitrogen was used as the carrier gas. The temperature was raised to the predetermined value. Once the preset temperature is reached, the steam generator was turned on to introduce pre-heated steam into the reactor and coal was injected. The off gases were passed through a water cold trap and then through the online GC analyzer.

Effect of Temperature: Table 2 summarizes the results of the coal gasification experiments conducted at different temperatures. 0.2 g of coal was gasified at different temperatures. The steam content used in these experiments was 82 %. It was observed that as the temperature is increased, the hydrogen content also increases. This increase was found to be the result of both – increased conversion of coal and enhanced water gas shift reaction. The latter is evident from the fact that as the temperature increased to 800 °C no carbon monoxide is observed in the resulting gases.

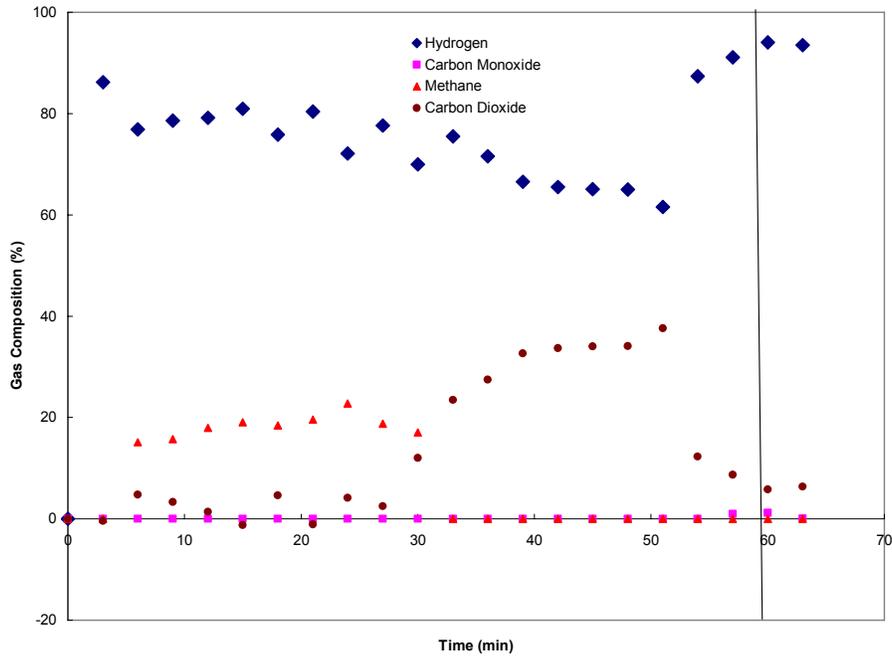


Figure 3: Outlet gas Composition for catalyst:CDRM ratio of 1:12

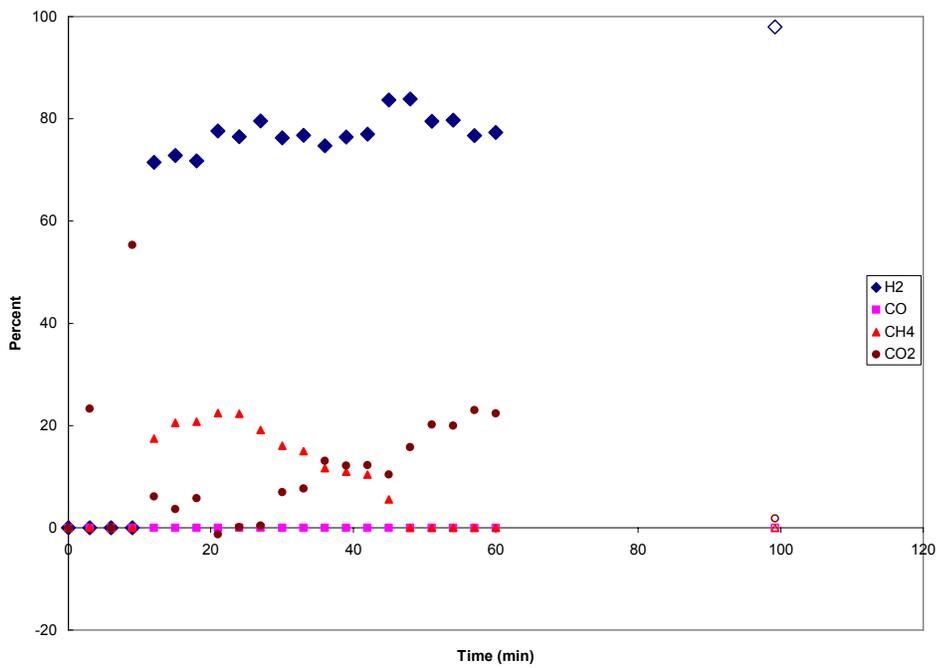
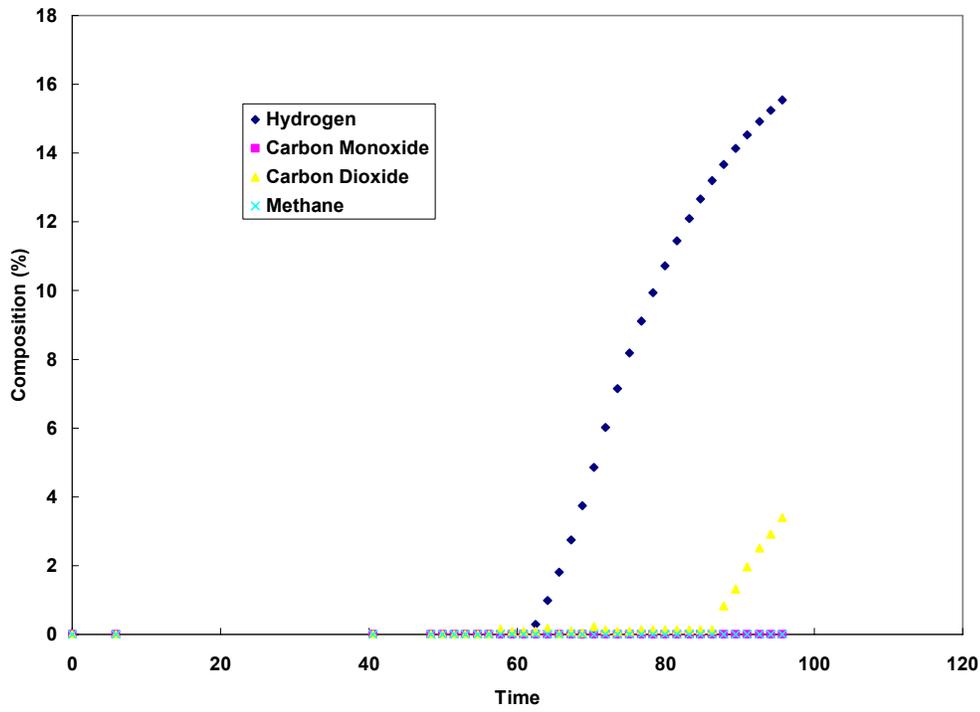
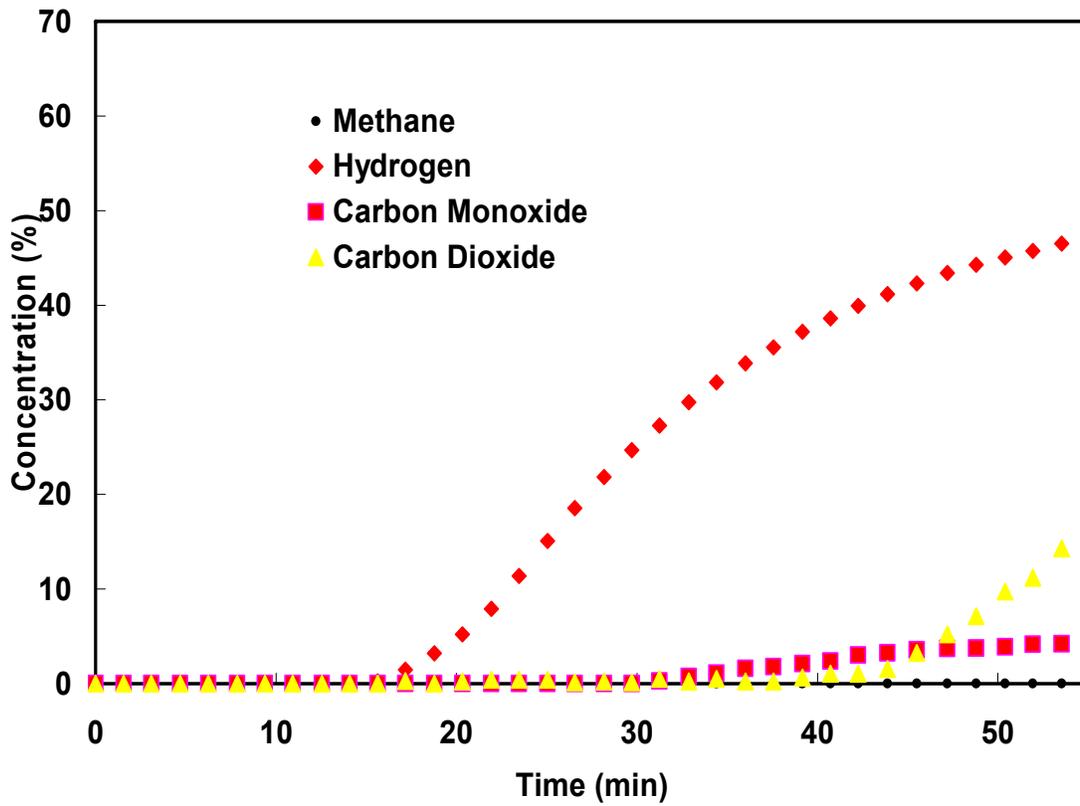


Figure 4: Outlet gas Composition for catalyst:CDRM ratio of 1:36



(a) 5 % syngas



(b) 50 % syngas

Figure 5

Effect of syngas content, gas flow rate – 45 ml/min

Table 2 Effect of Temperature

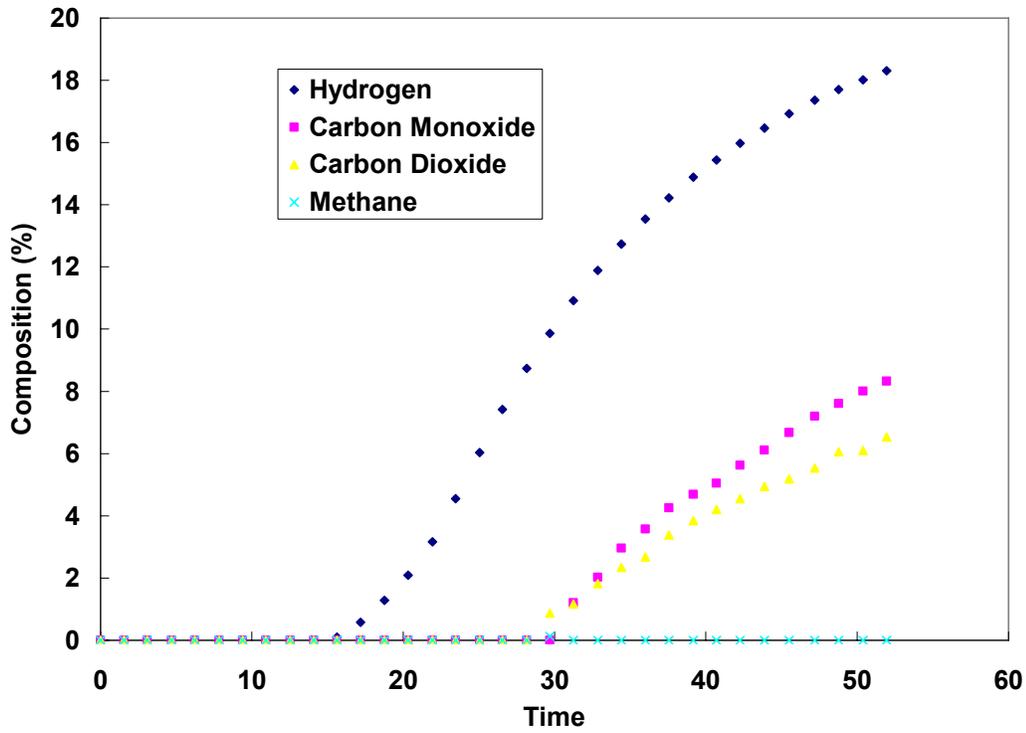
Temp °C	H ₂ %	CO %	CO ₂ %	CH ₄ %	Total moles	Conversion %
700	34.23	28.27	13.22	24.11	0.007	18.05
750	70.71	12.47	14.08	2.73	0.014	36.09
800	83.63	0.00	15.63	0.74	0.02	37.59
900	85.11	0.00	14.89	0.00	0.0252	41.23

Effect of Steam: Table 3 summarizes the data on the effect of steam on the coal conversion and the product gas distribution. 0.2 g of coal was gasified at 750 °C. It was seen in the table that an increase in the steam content results in a decrease in CO content (due to an increase in the degree of the water gas shift reaction) as well as a decrease in the methane content (due to steam reforming). The total amount of gases evolved also increased with an increase in the steam content.

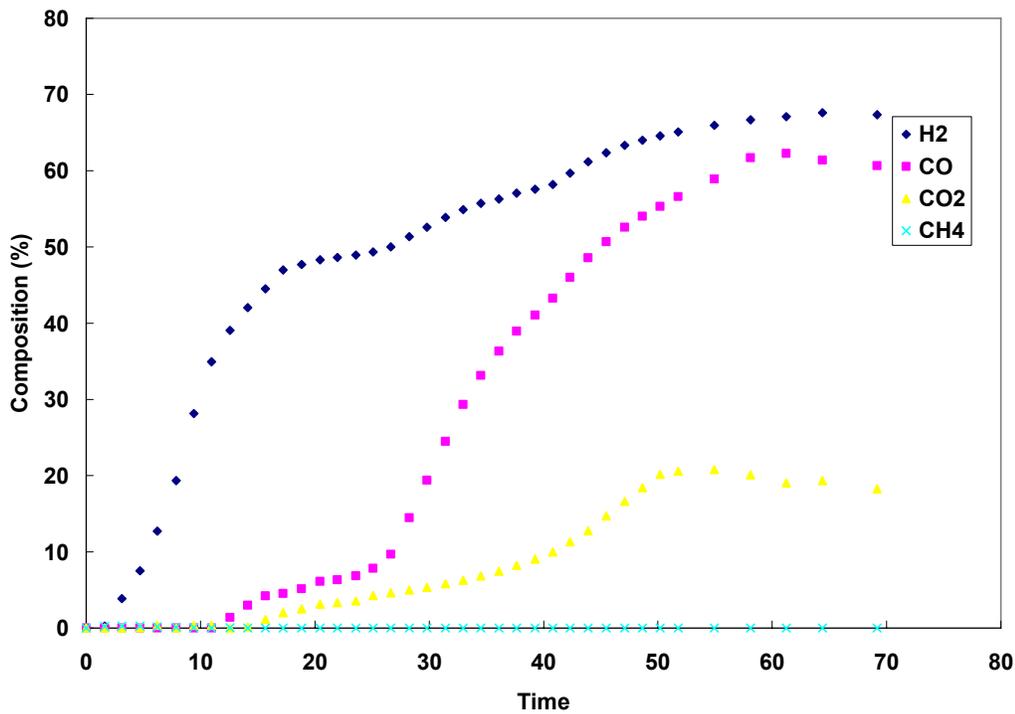
Effect of Coal Loading: The optimal amount of coal for maximizing the gasification yield was identified by running steam gasification experiments (82 % steam) at 750 °C. The data from these experiments are presented in Table 4. Experiments with 0.4 and 0.5 g of coal are not reported since it resulted in a large amount of tars and hydrocarbon formation.

Effect of solids addition: A comparison of pyrolysis, steam gasification, catalysts addition and catalysts and CDRM addition during steam gasification is shown in Table 5 and Figure 24. The experiments were conducted at 750 °C. 0.2 g of coal was used for these experiments. The table contains the cumulative product distribution at the end of 1 hr. It can be clearly seen there that CDRM presence increased H₂ content while CO content was decreased.

Effect of Catalyst Loading: Table 6 lists the outlet gas compositions for different amount of catalyst added. No CDRM was used for these experiments. It was observed that an increase in catalyst loading results in a decrease in the hydrogen content (initial water formation during reduction of iron oxide). However, the CO content and the H₂S content also decreased with an increase in catalyst loading. The effect of the catalyst on the gasification process was also observed by the increase in the gas yield due to its addition. Experiments were also conducted to evaluate the effect of catalyst loading in the presence of CDRM (in the ratio catalyst:CDRM = 1:3). No CO was observed at a catalyst loading of 0.56 g, while complete H₂S removal was obtained at a catalyst loading of 1.12 g. Since 0.05 g of coal was used, the catalyst to coal ratio for complete CO and H₂S removal was 44:1. 99.74 % pure hydrogen was produced under these conditions. It must be noted that the use of 1.68 g of CDRM with 0.05 g of coal yielded significant amount of CO and H₂S. Thus, the CO₂ acceptor process alone is not sufficient for complete impurity removal from coal derived syngas.



(a) 20 % syngas



(b) 50 % syngas

Figure 6 Effect of syngas content, gas flow rate – 100 ml/min

Table 3 Effect of Steam Content

Steam	H ₂	CO	CO ₂	CH ₄	Total	Conversion
%	%	%	%	%	moles	%
0	58.03	19.38	14.76	7.83	0.007	17.66
59	58.76	20.36	17.63	3.25	0.008	25.22
82	70.71	12.47	14.08	2.73	0.014	36.09
91	78.49	0.00	21.51	0.00	0.02	63.85

Table 4 Effect of Coal Loading

Coal	H ₂	CO	CO ₂	CH ₄	Total	Conversion
gm	%	%	%	%	moles	%
0.05	59.64	22.33	15.56	2.21	0.0028	51.88
0.1	61.18	17.87	18.27	2.68	0.0085	44.05
0.2	70.71	12.47	14.08	2.73	0.014	36.09

Table 5 Effect of solids addition

Steam	catalyst	CDRM	H ₂	CO	CO ₂	CH ₄	Total	Conversion
%	gm	gm	%	%	%	%	moles	%
0	0	0	58.03	19.38	14.76	7.83	0.007	17.66
82	0	0	70.71	12.47	14.08	2.73	0.014	36.09
82	0.56	0	68.31	2.46	27.69	1.55	0.0252	63.32
82	0.56	1.68	80.24	0.01	18.84	0.90	0.0113	93.22

Table 6 Effect of catalyst addition alone

catalyst	H ₂	CO	CO ₂	CH ₄	H ₂ S	Total	Conversion
gm	%	%	%	%	%	moles	%
0	59.64	22.33	15.56	2.21	0.26	0.0028	51.88
0.28	63.65	1.32	33.34	1.53	0.16	0.0070	79.98
0.56	52	0.19	46.123	1.68	0.007	0.006	69.84
1.12	42.72	0	55.47	1.82	0	0.0032	49.73

Effect of CDRM Loading: Table 8 contains the data on the cumulative outlet gas composition as a function of the CDRM loading for 0.56 g of catalyst loading. Increasing the CDRM loading resulted in an increase in the hydrogen purity, however, the H₂S removal was not complete due to the low catalyst loading.

HYDROGEN ENRICHMENT – SOLIDS REGENERATION

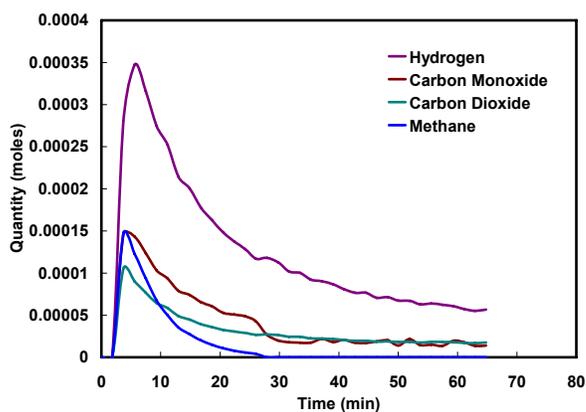
Hydrogen Enrichment – Solids Regeneration experiments were conducted for a catalyst loading of 0.84 and a CDRM loading of 1.68. The coal loading was 0.05 gm and the temperature and steam content were 750 °C and 82 %, respectively. One cycle of enrichment followed by regeneration in air and a second cycle of enrichment was studied. No change in the activity as evidenced by the outlet gas composition and total gas yield was observed.

As a result of these studies the following operating conditions are suggested: Temperature – 750 °C, Steam content – 82 %, catalyst:coal ratio – 44:1, catalyst:CDRM – 1:6. In addition, it is suggested that synthesized CDRM be used instead of the commercially available dolomite.

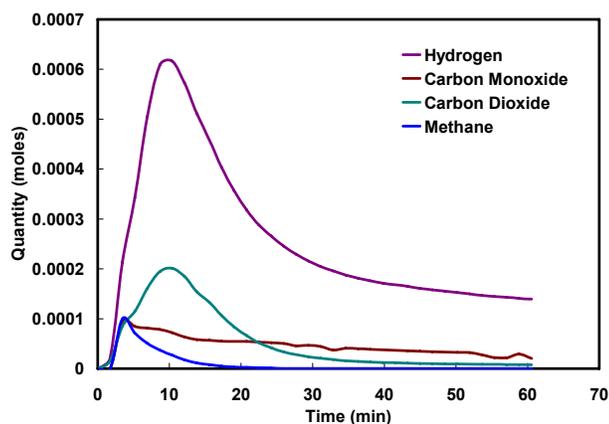
CONCLUSIONS

The following conclusions were made from the analysis of the data

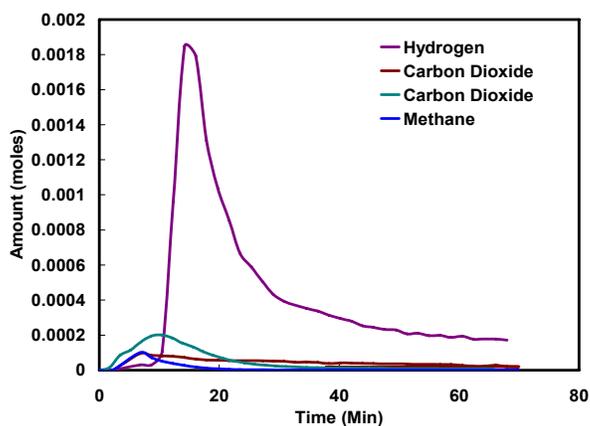
- 1) Suitable catalyst for Boudouard reaction was identified.
- 2) When used as a separate unit operation, the process should be operated at 800 °C
- 3) High residence time and high syngas content or low residence time and low syngas content should be used.
- 4) The addition of steam enhances the efficiency of CO removal.
- 5) The preferred catalyst to CDRM ratio is 1:3.
- 6) Suggested operating conditions for simultaneous gasification-enrichment: Temperature – 750 °C, Steam content – 82 %, catalyst:coal ratio – 44:1, catalyst:CDRM – 1:6.
- 7) The efficiency of separation did not decrease as a result of one enrichment-regeneration cycle.



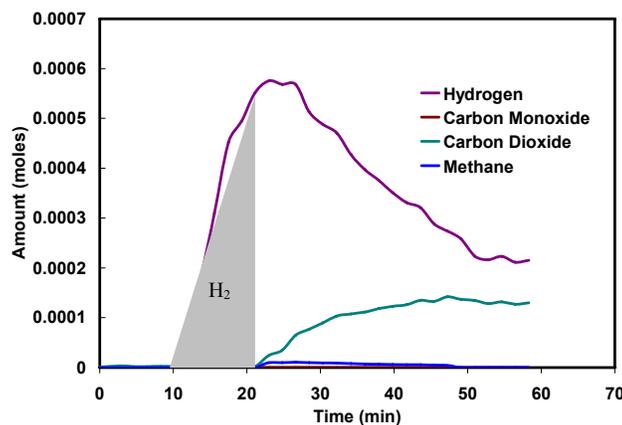
Pyrolysis of 0.2 g coal



Gasification of 0.2 g coal (82 % steam)



Steam (82 %) +Coal (0.2 g) + catalyst (0.56 g)



Steam (82 %)+Coal (0.2 g)+catalyst (0.56 g)+CDRM (1.68 g)

Figure 24 Separation of coal gasification products for high purity hydrogen: Carrier Gas – N₂ at 33 mL/min, Temp = 750 °C.

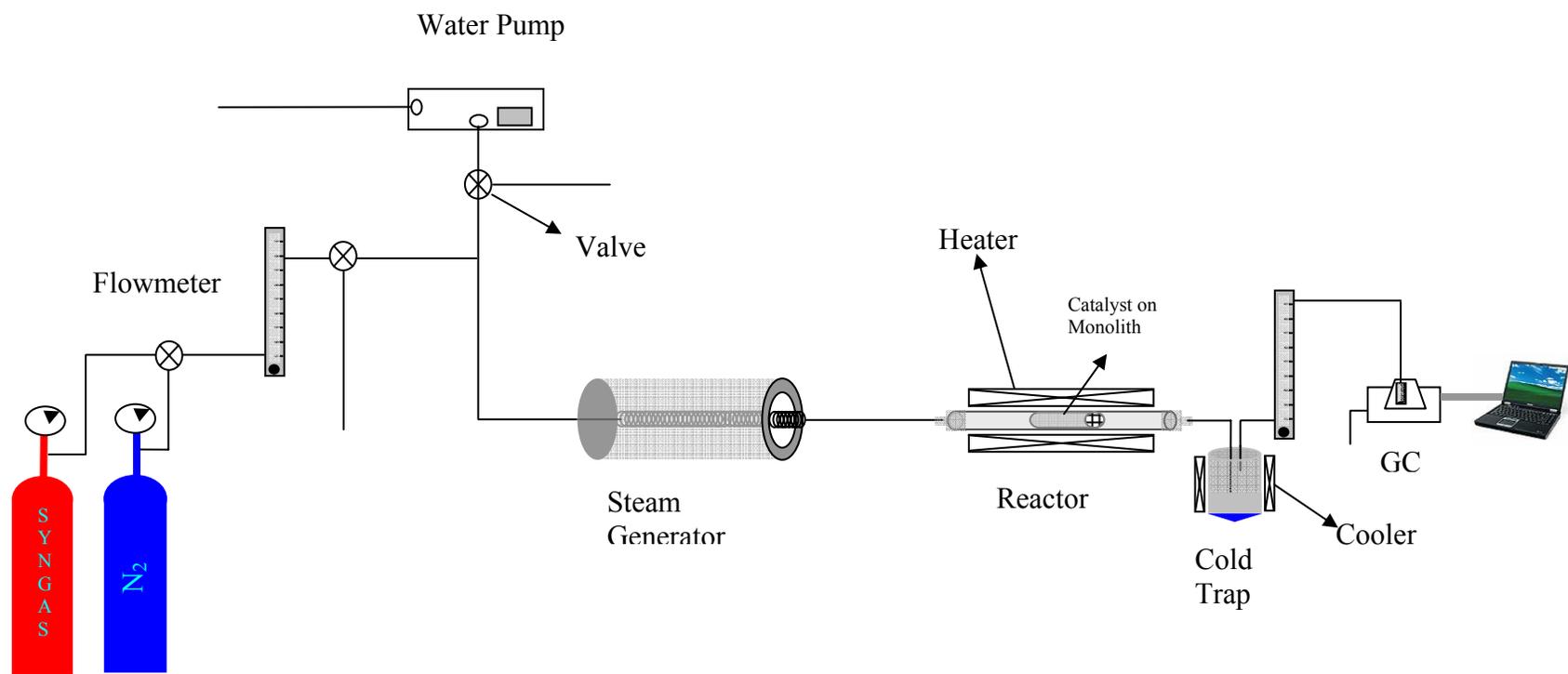


Figure 2 Schematic Diagram of the System

Table 7 Effect of iron oxide (catalyst:CDRM = 1:3)

catalyst	CDRM	H ₂	CO	CO ₂	CH ₄	H ₂ S	Total	Conversion
gm	gm	%	%	%	%	%	moles	%
0.28	0.84	61.53	0.42	37.13	0.83	0.086	0.0056	66.87
0.56	1.68	84.15	0	15.73	0.11	0.0017	0.0031	36.70
0.84	2.52	93.27	0	6.72	0.1	0.0005	0.0025	18.34
1.12	3.36	99.74	0	0.25	0	0	0.0023	9.25

Table 8 Effect of CDRM addition

catalyst	CDRM	H ₂	CO	CO ₂	CH ₄	H ₂ S	Total	Conversion
gm	gm	%	%	%	%	%	moles	%
0.56	0	52	0.19	46.12	1.68	0.007	0.0062	69.84
0.56	0.56	57.65	0	40.74	1.49	0.12	0.0051	65.14
0.56	1.12	54.75	0	43.53	1.41	0.31	0.0039	44.66
0.56	1.68	84.15	0	15.73	0.12	0.0017	0.0031	36.71
0.56	3.36	97.95	0	0.22	1.74	0.0839	0.0026	10.62