ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Optimization of Hydrogen Production from Coal – Alkali Interaction

Kumar G,*[2] Atma Ram Singh[1], S Srivastava[1], S K Srivastava[1]

[1] Central Institute of Mining & Fuel Research, Digwadih Campus, Dhanbad, PO. FRI, Dhanbad -828108, Jharkhand, India.
[2] BIT Sindri, P.O. Sindri Institute, Dhanbad – 828 123, Jharkhand, India.

ABSTRACT

Coal is an important source of energy and it has got remarkable effect when it is treated with alkali. The world's recoverable coal reserves contain about 3×10^{10} tons of hydrogen. "Hydrogen Economy' is a vision for future in with hydrogen replaced fossil fuels to reduce dependence on non-renewable energy and to cut down the environmentally harmful emissions. For this technology, hydrogen is mostly produced from hydrocarbons. Therefore, many researches have been conducted on hydrogen production from hydrocarbons to find the most economical, efficient and practical method of producing hydrogen as substitute of fossil fuel.Studies on production of environment friendly clean and green fuel hydrogen from different ranks of coal in presence of different alkalis were carried out under different reaction conditions. The yield of hydrogen depends upon the rank of coal as well as on the nature of alkali beside reaction temperature and other parameters. Amongst the various ranks of coals used, the maximum yield of gas obtained was 3.2 liters/10gm of coal with 80 %(v/v) of hydrogen from medium rank Swang coal (carbon-85.5%). Effects of temperature, particle size and coal-alkali ratio on the yield and quality of gas obtained from coal-alkali reaction were studied. It was found that the optimum reaction temperature is 600^0C while 1: 1.3 is the optimum coal-alkali ratio and x72 BS mesh is the particle size for maximum yield and quality of fuel gas. Under optimum reaction condition, the yield of hydrogen and methane was 80% and 12% (v/v) respectively while in the absence of alkali the same were 18.8% and 38.8 % (v/v) respectively The yield of the product gas obtained on pyrolysis of Swang coal in absence of alkali was 0.7 liters / 10 gm of coal. Thus, on addition of alkali, the product gas yield increases about five folds while the yield of hydrogen enhanced from 0.1316 liter to 2.56 liter i.e. about 20 times. The residual char was washed with water till alkali free. Alkali was recovered in the form of carbonates. The char was found to be extremely reactive towards steam gasification to generate CO + H_2.

Keywords : Pyrolysis, Alkali, Char, Fuel Gas

***Corresponding author**
Email : drgkumar12@gmail.com

INTRODUCTION

Production of environment friendly clean and green fuel hydrogen from coal-alkali interaction has been a challenging area of research from the very beginning [1 – 2]. Pyrolysis of coal at 600^{0}C resulted in product gas comprising of methane and hydrogen besides CO_2, C0 and other hydrocarbons. But when alkali is added to coal, then pyrolytic reactions are moderated in such a manner that the tar was converted into gas, CO_2, CO was absorbed hence the product gas contained only- the major H_2, CH_4, and in traces other hydrocarbons. Thus on addition of alkali, the yield of the product gas & hydrogen gas yield enhanced enormously. Srivastava et.al. [1, 2] studied effects of temperature, rank of coal, size of coal and role of different alkalies on the yield and quality of gas obtained from coal-alkali reaction. It is well known that the two coals of different ranks show their different properties due to their different chemical and physical properties [3, 4]. The present work is an extension of earlier work in this line.

MATERIALS AND METHODS

For coal-alkali reaction, one lignite from Neyveli and four different coals viz. Swang, Dakra Bukbuka, Jeypore and Mahuda were used. The various lignite /coal samples were crushed to x72 BS mesh size. The proximate and ultimate analyses were done following BIS method, and functional groups present in coal such as O_{OH}, O_{COOH}, f_a, f_{ha} and f_{ali} were estimated in the laboratory.

The coal-alkali reaction was carried out in a cylindrical mild steel (MS) reactor (200 mm length and 30 mm diameter) closed at one end and the other end of the reactor was closed by threaded MS cap fitted with an L shaped steel pipe outlet for exit of product gas and tar vapor if any, which is connected to the carbuoy in which gas was collected by water displacement method. The carbuoy contained saturated brine solution. A manometer was fitted with carbuoy.

10 gm. of air dried coal/ lignite sample of desired size fraction was taken and mixed thoroughly with desired concentration of alkali and placed in the cylindrical reactor for the experiment. The reactor containing coal-alkali mixture was placed inside the furnace. Heating of reactor was started from room temperature to 600^{0}C at the rate of 10^{0}C/min. till gas evolution ceased. The evolved product gas was collected, cooled at room temperature and the volume of gas was noted at NTP. The gaseous mixture was analyzed by Gas Chromatograph. Finally the alkali was recovered from the residual char by washing with hot water till alkali free. The residual char was dried at 110^{0}C till constant weight which was found to be highly reactive towards steam gasification.

RESULTS AND DISCUSSION

Table-1 summarizes the proximate and ultimate analyses of coal / lignite. From this table, it is observed that the moisture content in Dakra-Bukbuka coal and Neyveli lignite are high as it is of low rank with respect to other coals. Jeypore coal contain 4.13% total sulphur which is an abnormal high sulphur Assam coal where part of oxygen is replaced by sulphur as compared to the normal coal of the same rank. The ash content of Neyveli lignite and Jeypore coal are low i.e 4.0 ± 0.5 and the rest of the coal is in between 14.7 and 18.0% the rank of coal varies from lignite to coking coal. In the present case Neyveli is lignite, Dakra-Bukbuka & Jeypore coals are sub-bituminous, Swang coal is medium coking coal and Mahuda is coking coal The hydrogen content of Mahuda coal is 4.8% while for all other coals/lignite it is >5% on dry mineral mater free basis. Amongst all the coals/lignite, Swang coal is having higher nitrogen content ie 2.8%. The oxygen percent of lignite is higher than other coals as it is of low rank.

Table 1: Proximate and ultimate analyses of coal/lignite (on dmf) basis

Coal/Lignite	Proximate (%)				Ultimate (%)				
	M	A	VM	FC	C	H	N	S	O
Neyveli/lignite	37.3	3.4	54.5	45.5	71.30	5.0	0.8	0.74	22.06
Dakra Bukbuka coal	10.0	18.0	48.4	51.6	79.49	5.4	1.6	0.66	12.86
Jeypore Coal	2.1	4.5	42.3	57.7	79.7	5.8	1.1	4.13	9.3
Swang Coal	2.5	14.7	31.4	68.6	85.49	5.5	2.8	0.8	6.01
Mahuda Coal	1.9	16.0	39.1	60.9	89.6	4.2	2.4	0.42	3.37

Table -2 summarizes the data on pyrolysis of lignite/coals at 600^0C and in presence of alkali with 1:1.3 coal/alkali ratio i.e. under optimum reaction conditions. It is observed that the volume of the product gas obtained with Jeypore and Swang coals are practically the same i.e 732 ± 7 ml where as the volume of product gas obtained using other coals varies from 980 ml/10 gm to 650 ml/10gm from lignite to Mahuda coal. It is observed from the table that the highest amount of CO_2 came from Neyveli lignite due to the presence of higher percent of -COOH functional groups in lignite, which yielded CO_2 during pyrolytic reaction. Similarly the percent yield of CO in the product gas decreases from 19.3% to 3% from lignite to high rank coal Mahuda. The hydrogen content in the product gas is 19 ± 1 for all the coals except for lignite where it is 14.1%. Similarly methane content for Neyveli lignite is 24.2% and in case of rest of the coals, it is 40.5±1.5% except Jeypore coal, where it is 27.1%. This is due to the reason that sulphur takes away hydrogen to form H_2S. The percent composition of H_2 and CH_4 gases in the product gas in case of all coals/ lignite can be explained on the basis of dehydrogenation and demethylation reaction occurring during pyrolysis [5, 6].

Table 2: Yield and Quality of gas obtained from pyrolysis of 10 gm of different Coal/lignite at 600^0C

Coal/ Lignite	Volume gas at NTP in ml.	% Composition of the Product Gas										
		H_2	CH_4	CO	CO_2	N_2	O_2	C_2H_6	C_2H_2	C_3H_6	C_3H_8	C_4H_{10}
Neyveli lignite	980.0	14.1	24.2	19.3	30.7	11.7	---	---	---	---	---	---
Dakra Bukbuka coal	732.0	18.3	38.7	13.0	13.7	8.0	---	5.8	1.0	---	1.1	---
Jeypore coal	725.0	18.6	27.1	10.6	14.0	20.4	2.9	3.2	1.0	1.0	.9	.07
Swang coal	739.5	18.8	38.8	3.8	1.2	21.3	5.4	6.1	1.5	1.6	1.1	---
Mahuda coal	680.0	19.8	37.3	3.0	0.9	13.6	---	9.0	1.3	1.0	1.1	0.6

Table-3 presents the data on the volume and composition of gaseous products obtained from coal/lignite sodium hydroxide reaction under optimum condition. From the table, it is clear that no CO, CO_2 and higher hydrocarbons were obtained. Similarly no tar /liquor was obtained during the reaction. The CO_2 generated during pyrolysis reaction was absorbed by NaOH forming Na_2CO_3 hence CO_2 could not be obtained. Thus in the absence of CO_2, CO_2-C reaction does not take place to yield CO. The Tary material formed during pyrolysis was hydro-cracked to yield gaseous product hence tar/ liquor could not be obtained. Similarly the unsaturated hydrocarbon formed went on for addition reaction with hydrogen during the course of pyrolytic reaction to yield saturated hydrocarbon which further cracked (higher hydrocarbons) to yield methane and hydrogen. Thus enhancing the yield of hydrogen enormously in comparison to normal pyrolysis of coal at 600^0C. The reaction mechanisms of pyrolysis of coal thus change in presence of alkali as compared to the normal pyrolytic reaction of coal [7].

Table 3: Yield and quality of gas obtained from pyrolysis of 10 gm of different coals/lignite in presence of NaOH (coal: alkali ratio 1: 1.33 at 600^0C)

Coal/lignite	Volume of gas at NTP in ml	% composition of the product gas				
		H_2	CH_4	CO	CO_2	N_2
Neyveli lignite	2750	82.0	14.6	--	--	2.4
Dakra-Bukbuka coal	2900	85.0	10.5	--	--	3.0
Jeypore coal	2900	80.3	12.7	---	--	5.7
Swang coal	3132	79.9	12.5	---	--	6.5
Mahuda coal	2000	85.5	10.5	---	--	2.8

Table-4 presents the data on the effect of nature of alkali on the yield and quality of gas obtained from Swang coal-alkali reaction under optimum condition. Four alkalies were used for the purpose are Sodium hydroxide, sodium carbonate, calcined lime and calcium carbonate. It is observed from the table that the volume of product gas is just double in case of NaOH in comparison to other alkalis used. In case of NaOH , the hydrogen percent in the product gas obtained is 80%(v/v) which is very high but using alkali carbonate the hydrogen content in the product gas is reduced to less than double but simultaneously the methane gas percentage becomes higher by more than half. In case of carbonates as alkali, the CO and CO_2 were also present in the product gas amounting to about 20% (v/v). Higher hydrocarbons are also present in case of alkalies, other than NaOH, were used in coal-alkali reaction [6]

Table 4: Effect of nature of alkali on the yield and quality of gas obtained from 10 gm of Swang-coal under optimum reaction conditions

Coal/ Lignite	Volume gas at NTP in ml.	% Composition of the Product Gas										
		H_2	CH_4	CO	CO_2	N_2	O_2	C_2H_6	C_2H_2	C_3H_6	C_3H_8	C_4H_{10}
NaOH	3132	79.9	12.5	----	---		---	1.2	0.5	0.5	0.5	0.6
Na_2CO_3	1434	31.5	26.2	7.3	12.7	16.5	---	3.3	0.7	0.9	0.8	-
Calcined lime	1186	36.5	36.9	5.7	2.1	13.0	---	4.7	1.4	1.0	0.9	--
$CaCO_3$	1440	35.0	33.2	9.5	8.3	10.0	---	2.2	0.5	0.4	0.7	--

Table- 5 summarizes the data on the effect of different particle sizes of Swang coal at 600^0C temperature and 1 : 1.33 coal-alkali ratio on the yield and quality of obtained gas. It was observed from the table the yield of gas obtained from the sizes x72 BS Mesh is same as compare to that of x100BS Mesh. More over the composition of gaseous component is also same. If yield and quality of gas are same the it is better to use the coal particle size x72 to save mane power as well as the extra energy for making x100 BS mesh. So that x72 BS mesh size is considering as optimum coal particle size for better yield and quality of fuel gas [8-9].

Table 5: Effect of particle size of swang coal on production of fuel gases at optimum coal/alkali ratio (1 : 1.3) and reaction temp 600^0C

Size of coal	Vol.of gas% at NTP(in ml)	Composition of product gas									
		H_2	CH_4	CO	CO_2	N_2	O_2	C_2H_6	C_2H_4	C_3H_8	C_3H_6
X36	2832	72.6	14.1	-	-	12.5	-	0.9	0.9	0.3	0.1
X56	2904	76.8	13	-	-	9	-	1.1	0.1	0.3	-
X72	3132	79.3	12.5	-	-	5.5	-	1.2	0.2	0.4	0.4
X100	3200	80.0	12.6	-	-	5.2	-	1.2	0.2	0.2	0.4

CONCLUSION

It is concluded that the optimum conditions for coal-alkali reaction to generate hydrogen is coal: alkali ratio of 1:1.33, temperature 600^0C, most suitable alkali is NaOH, produces 3.2 liters of product gas with 80%(v/v) hydrogen from 10 gm of coal. The medium rank coal with carbon (C 85.5%) is suitable for hydrogen production during pyrolytic condition and functional groups such as –OH group play an important role in hydrogen production [10]. Higher the content of hydroxyl group, minimum is the hydrogen production. Hydrogen comes from dehydrogenation and demethylation of coal besides coalescence of aromatic rings. Alkali hydroxide yield more hydrogen while alkali carbonates yield more of methane.

REFERENCES

[1] Srivastava SK, Saran T, Sinha J, Ramachandran LV and Rao SK. Fuel Loldon 1988; 67:1683.

[2] Srivastava SK, Kumar A and Haque R. Fuel Science & Technology 1992; 11:111.

[3] Bellona Report. Hydrogen- Status and possibilities 2002. (http://www.bellona.com).

[4] Larsen JW, Li S. Hydrogen Donor Reactivity and Capacity of Coals. Energy Fuels. 1998; 12: 830-831.

[5] Larsen JW, Azik M, Lapucha A, Li S, Kidena K, Nomura M. Coal Dehydrogenation Using Quinones or Sulfur. Energy Fuels 2001; 15:801-806.

[6] Schobert HH, Song C. Chemicals and Materials from Coal in the 21st century. Fuel 2002; 81: 15-32.

[7] Andrésen JM, Morrison JL, Rusinko F, Zondlo JW, Stipanovich J, Winslow JC, Schobert HH. Am Chem Soc Div Fuel Chem 2003; 48:22-23.

[8] Wang YN and Rodrigues AE. Fuel 2005; 84:1778–1789.

[9] Liu S, Takahashi K, Uematsu K and Ayabe M. Applied Catalysis A: General 2005; 283:125–135.

[10] Cheekatamarla PK and Lane AM. Int J Hydrogen Energy 2004; 30:1277 – 1285.