ROLE OF AROMATIC AND HYDROAROMATIC HYDROGEN OF COAL WITH ALKALI FOR GENERATING CLEAN FUEL HYDROGEN

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ABSTARCT

Studies on pyrolysis of different ranks of coal viz. Jeypore (sub-bituminous), Swang (Bituminous), Dakra Bukbuka (Sub-bituminous), Mahuda (High rank) and Neyveli lignite (Lignite), in presence of different alkalies viz. Sodium hydroxide, sodium carbonate, calcined lime and calcium carbonate were carried out under different reaction conditions for the production of clean and green fuel hydrogen. Pyrolysis of different ranks of coals in presence of sodium hydroxide produces clean and green fuel hydrogen. Amongst the various coals used, the maximum yield of gas obtained was 3.2l/10 g of coal with hydrogen content of 80 % (v/v) from the medium rank Swang coal (carbon 85.5% on dmf basis). It was also observed that two coals of same carbon and hydrogen content exhibit different behavior due to their different chemical and physical makeup. For example, the coal which has rich vitrinite maceral produces better yield of hydrogen in comparison to other coals having more of inertinite maceral. Effect of temperature, nature of alkali, coal-alkali ratio, rank of coal, coal particle size etc. on the yield and quality of gas obtained from coal-alkali interaction were studied to find out optimum reaction conditions. It was found that 600^0C is the optimum temperature and 1 : 1.3 is the optimum coal : alkali ratio for this reaction. This paper reports the data obtained on five coals-four alkalies interaction under optimum reaction conditions.

No tarry product was obtained during the course of pyrolysis of coal in presence of alkali. Similarly, under optimum reaction conditions, no carbon monoxide and carbon dioxide were found as it reacted with alkali. It is well known that the hydroaromatic part of the coal is mainly responsible for production of tarry component during coal pyrolysis and CO & CO_2 are the products of coal pyrolysis. But addition of alkali changes the reaction mechanism of normal pyrolysis of coal in such a way that no tarry product was obtained. The active hydrogen of methylene interacts with hydrogen of sodium hydroxide to

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form hydrogen gas at the temperature range from 350^0C to 400^0C. Aromatic hydrogen also participates in the same fashion but the elimination temperature range for aromatic hydrogen is higher than that of active methylene groups. Under optimum reaction conditions, the yields of hydrogen and methane were 500 m^3 and 75 m^3 per ton of coal, respectively. The recovery of alkali was 87%. Part of alkali has reacted with the mineral matter. The results have been interpreted in terms of macerals, functional groups, aromaticity and hydroaromaticity of coal.

INTRODUCTION

Production of environment friendly hydrogen from coal-alkali interaction has already been reported for few coals in literature[1,2]. Pyrolysis of coal at 600^0C results in the evolution of product gas comprising of about 50% methane and 30% hydrogen. But when alkali is added to coal, it moderates the pyrolytic reactions in such a way that the yield of hydrogen gas enhanced to 82% by volume with evolution of gas from the same quantity of coal by about ten times in comparison to normal pyrolysis of coal. Effects of temperature, alkali to coal ratio, nature of alkali, coal particle size and rank of coal on the quality and yield of gas obtained from coal-alkali interaction were studied in the past. It is worth mentioning here that the coal rank may be similar in two coals but in terms of reactivity, they may differ e.g., coal having more vitrinite content will be more reactive than the coal having more inertinite content. Thus, macerals in coal plays an important role during reaction. It can modify the product gas composition. Similarly, functional groups also play an important role in deciding mode of the reaction and hence, the composition of the gaseous products. As also variation in the aliphalicity, alicyclicity or hydroaromaticity and aromaticity will change the product pattern composition. So far no work has been done in this respect. In order to fill this gap, effect of various functional groups present in the coal and also vitrinite content, aliphaticity, aromaticity and hydroaromaticity on the yield and quality of gas obtained from coal-alkali interaction were studied and the results thus obtained formed the basis of this paper.

EXPERIMENTAL

Methodology

Experimental setup for carrying out coal-alkali reaction

For coal-alkali reaction, one lignite from Neyveli and four different coals viz Swang, Dakara Bukbuka, Jeypore and Mahuda were used. The various lignite/coal samples were crushed to x72 mesh size. The proximate and ultimate analyses were done following BIS

method, and functional groups present in coal such as hydroxyl (O_{OH}), Carboxyl (O_{COOH}), aromaticity (f_a), hydroaromatic (f_{har}) and aliphaticity (f_{ali}) were determined in the laboratory. The coal-alkali reaction was carried out in a cylindrical mild steel reactor of size (200 mm length and 30 mm diameter) closed at one end. Open end of the reactor was closed while carrying out the reaction using threaded MS cap fitted outside having an L shaped mild steel pipe outlet for exit of product gas and tar vapor (5 mm internal diameter) connected to the carbuoy containing saturated brine solution in which product gas was collected. The other end of the carbuoy was connected to a manometer. The complete experimental setup is shown in Fig. 1. The tar catcher was kept in an ice bath to trap the tar formed, if any, and allow only the gaseous product to pass into the carbuoy. Energy regulator was used to control the temperature, which was measured by pyrometer. The reactor was kept in a horizontal furnace slightly elevated at the open end side of the reactor.

Preparation of coal-alkali paste for charging the reactor

10 g of air-dried coal/lignite of desired size fraction was taken and mixed thoroughly with the desired concentration of alkali and placed in the cylindrical MS reactor for the experiment. The reactor containing coal-alkali mixture was placed inside the furnace after fitting the threaded MS cap and connections made as mentioned above. Heating of the reactor was done at the rate of $10^0C/min.$ from room temperature up to the desired temperature after that it was maintained constant till gas evolution ceased. The evolved product gas was collected in a carbuoy over saturated brine solution.

Collection of gas samples and its analysis

The product gas was collected in the carbuoy by the displacement of saturated brine solution. The gaseous mixture, which was collected in the carbuoy, was cooled at room temperature. The volume of gas at room temperature and atmospheric pressure was noted and finally the gas volume was calculated at NTP. The gaseous mixture was analyzed by gas chromatograph.

Recovery of alkali

Alkali was recovered from the residual char by washing with minimum quantity of hot distilled water until it was free from alkali, and the alkali solution was titrated against standard oxalic acid solution using methyl orange and phenolphthalein as indicator, respectively for the estimation of alkali as carbonate and as hydroxide. The washed char was then dried in an air oven at 110^0C till constant weight, equilibrated at room temperature and sent for analyses (Proximate and Ultimate). The residual char was found to be highly porous and had higher moisture content possibly due to presence of minute traces of alkali, which

was difficult to remove even by repeated washing with hot distilled water. The char had high reactivity towards steam gasification[3].
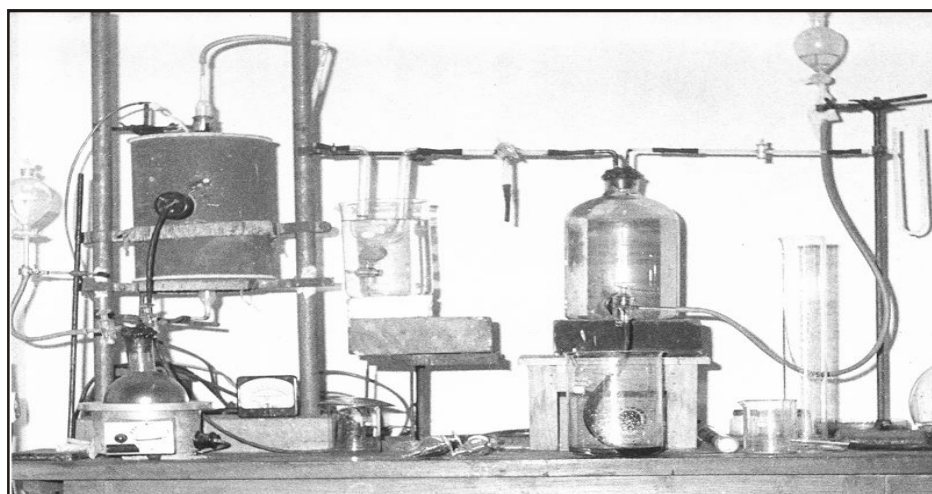

Fig. 1: Experimental Setup

RESULTS AND DISCUSSION

Table 1 summarizes the proximate and ultimate analysis of Dakra Bukbuka, Jeypore, Swang and Mahuda coals, and Neyveli lignite on dry mineral matter free basis. It can be observed from the table that the moisture content of Dakra Bukbuka coal and Neyveli lignite are high as they are non-coking coals/lignite but for rest of the coals, it is in between. Jeypore coal (4.13%. total sculpture) is an abnormal high sculpture Assam coal, where part of 'O' is replaced by 'S' as compared to normal coal of the same rank. The ash content of Neyveli lignite and Jeypore coal are low i.e. 4.0 ± 0.5 and for rest of the coals, it is between 14.7 and 18.0%. The volatile matter content of all the coals and lignite are in the range 26-32.5% on air dried basis. The sculpture content of Jeypore coal is high while that of other coals are < 0.7% (on dmf basis). The rank of coal varies from Neyveli lignite to sub-bituminous (Dakra Bukbuka and Jeypore coal) to high rank low volatile bituminous Swang coal (medium coking coal) to coking coal Mahuda. The hydrogen content for Mahuda coal is 4.8% while for all other coals/lignite, it is $\geq$ 5% on dmf basis. The nitrogen content for lignite and sub-bituminous coal as above are in the range 0.8 to 1.6% while that of Swang coal and Mahuda coal are 2.8% and 2.4%, respectively (on dmf). Neyveli lignite has high oxygen content followed by sub-bituminous and bituminous coal. The fixed carbon value on air dried basis is in the range 27% to 55%.

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	71.3	5.0	0.8	0.70	22.2
Dakra Bukbuka Coal	10.0	18.0	48.4	51.6	79.5	5.4	1.7	0.70	12.7
Jeypore Coal	2.1	4.5	42.3	57.7	79.7	5.8	1.1	4.10	9.3
Swang Coal	2.5	14.7	31.4	68.6	85.5	5.5	2.8	0.80	5.4
Mahuda Coal	1.9	16.0	39.1	60.9	89.6	4.2	2.4	0.40	3.4

Table 2 presents the analysis of oxygen containing functional groups present in coal/lignite such as O_{OH} and O_{COOH}, and distribution of carbon, which are in the forms of aromatic, hydroaromatic and aliphatic i.e. known as aromaticity, hydroaromaticity and aliphaticity, respectively. Generally, estimation of oxygen containing functional groups means the distribution of oxygen as O_{OH} and O_{COOH}, which played important role during coalification & etherial oxygen and carbonyl (O_{CO}), which did not alter much from Neyveli lignite to Mahuda coal. The aliphaticity of Neyveli lignite, Dakra Bukbuka and Jeypore coals are practically same i.e. 8-8.5%, and that of Swang, Mahuda coals are 7.0%. In Mahuda and Swang coals, the aromaticity values are higher i.e. 70% and 82%, respectively in comparison to all other coals/lignite, which are in the range of 60 to 65.5%. Mahuda coal is coking while Swang coal is semi-coking and coking property of coal is not a linear function of hydroaromaticity. The values of hydroaromaticity are 11%, 23%, 26%, 29% and 32% for Mahuda, Swang, Dakra Bukbuka, Neyveli lignite and Jeypore coals, respectively. The higher hydroaromaticity value of Jeypore coal result in yielding twice the quantity of tar in comparison to a coal of similar carbon percent on low temperature carbonization. It is well known that hydroaromatic part of the coal is directly related to the tar yield. It is also known that the methane and hydrogen comes from demethylation and dehydrogenation of coal matrix and aromatic ring coalescence, respectively. Since H/C ratio increases up to 83-84% and then it becomes constant; maximum yield of hydrogen expected would be at 83-85% carbon level of coal. Hence, Swang coal yielded maximum hydrogen. Below 83-85% carbon level, the hydrogen evolved from the aromatic ring coalescence reacts with – OH group to yield water. –COOH group yields carbon dioxide. Hence, in lignite or coals of rank < 83% carbon, quantity of hydrogen evolved is less as is evident from these data.

Table 2: Estimation of functional groups present in coal and distribution of carbon in coal/ lignite (%)

Coal/ Lignite	O_{COOH}	O_{OH}	f_{ar}	f_{har}	$f_{ali} (C_{CH_3})/C$
Neyveli/Lignite	5.6	6.6	62.5	29.0	8.5
Dakra Bukbuka coal	1.2	5.6	65.5	26.0	8.5
Jeypore coal	0.5	5.0	60.0	32.0	8.0
Swang coal	0.2	2.5	70.0	23.0	7.0
Mahuda coal	0.14	2.1	82.0	11.0	7.0

Table 3 summarizes the data obtained on pyrolysis of lignite/different ranks of coal at 600^0C and 1 : 1.3 coal/alkali ratios i.e. under optimum reaction conditions. It is observed from the table that the volume of the product gas varies from 980 mL/10 g of lignite feed to 680 mL/10 g of Mahuda coal feed. Practically, similar volume of gas was obtained viz 732 ± 7 mL/10 g feed from rest of the coals. It can be observed that Neyveli lignite yields highest amount of CO_2, this is because number of -COOH groups are present in the lignite, which on pyrolysis broke to yield CO_2. This is followed by sub-bituminous and bituminous coals because as the rank of coal increases, number of - COOH groups decreases. Similarly, % CO in the product gas gradually decreases from 19.3% for lignite to 3% for Mahuda coal. 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 for rest of the coals, it is 40.5 ± 1.5% except Jeypore coal, where it is 27.1%. This may be due to the taking away of the CH_4 by presence of high sulfur in Jeypore coal to yield H_2S[4,5]. The percent volume of H_2S was not estimated in gaseous mixture. The occurrence of oxygen and nitrogen in the product gas may be explained due to the presence of residual air initially in the reactor system. The composition of H_2 and CH_4 gases in the product gas in case of all the lignite/coals can be explained on the basis of dehydrogenation and demethylation reaction occurring during pyrolysis. CO is produced during low temperature carbonization of coal/lignite. Small amount of oxygen present in the reactor system as stated above may react to produce CO. Similarly, other higher hydrocarbons are also present (Table 3) which are normally found during low temperature carbonization of coal as reported in literature. No attempt was made to collect, weigh and analyze the tar/liquor obtained during pyrolytic reaction.

Table 3: Yield and quality of gas obtained from pyrolysis of lignite/different rank of coal at 600^0C

Coal/ Lignite	Volume of gas at NTP (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 4 sets up data on volume and composition of gaseous products obtained from coal/lignite–sodium hydroxide reaction under optimum reaction conditions. It can be observed from the table that in presence of alkali, no CO, CO_2 and higher hydrocarbons were obtained. Similarly, no tar/liquor was obtained during this reaction. The CO_2 generated during pyrolysis reaction was absorbed by NaOH forming Na_2CO_3 and hence, CO_2 could not be obtained in product gas. In the absence of CO_2, no CO_2-C reaction occurred to yield CO. The tar formed during pyrolysis reaction was hydro-cracked to yield gaseous products and hence, tar could not be obtained. Similarly, the unsaturated hydrocarbon adds hydrogen formed during the reaction, which further cracked to yield methane and hydrogen; thus, enhancing the yield of hydrogen enormously in comparison to pyrolysis of coal at 600^0C in absence of alkali. As explained above, the yield of the gaseous products have gone up about ten times. The mechanism of the pyrolysis reaction has changed in pyrolytic reaction in presence of alkali as compared to the normal pyrolysis reactions. The ratio of O_2 and N_2 is not 1 : 4 because as some of the oxygen reacted with some of the carbon in coal forming CO. It is well known that the tarry component obtained during pyrolysis is mainly due to hydroaromatic part of the coal. From the Tables 2 and 4, it is clear that the production of hydrogen by coal-NaOH interaction is not a linear function of hydroaromaticity of coal.

Table 5 presents the data on effect of nature of alkali on the yield and quality of gas obtained from Swang coal-alkali reaction under optimum reaction conditions. Four alkalies viz. sodium hydroxide, sodium carbonate, calcined lime and calcium carbonate were used for the purpose. It can be observed from the table that with NaOH, the volume of the product

gas is more than double in comparison to the corresponding volume of the product gases obtained using other three alkalies under similar reaction conditions. With hydroxide as standard alkali, the amount of the hydrogen present in the product gas is very high i.e. 80 vol. % but with carbonate as alkali, the hydrogen content in the product gas is reduced to less than half. But simultaneously, the methane percentage became higher by more than double. In case of carbonate as alkali, CO and CO_2 were also present in the product gas amounting to about 20 % (v/v). The calcined lime yield about 8 % (v/v) CO + CO_2. Higher hydrocarbons were also present in case of all the alkalies except sodium hydroxide.

Table 4: Yield and quality of gas obtained from pyrolysis of 10 g of different coals/lignite in presence of NaOH (coal : alkali), 1 : 1.33 at 600^0C

Coal/Lignite	Volume of gas at NTP (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	3232	79.9	12.5	---	--	6.5
Mahuda coal	2000	85.5	10.5	---	--	2.8

Table 5: Effect of nature of alkali on the yield and quantity of gas obtained from 10 g of Swang-coal under optimum reaction conditions

Coal/ Lignite	Volume gas at NTP (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	----	---	6.5	---	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	--

Reactions

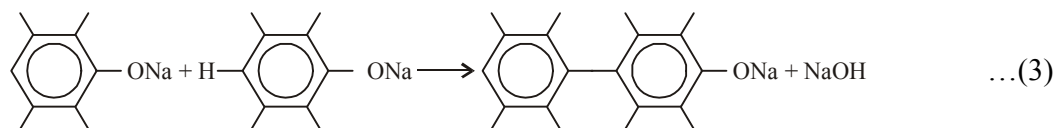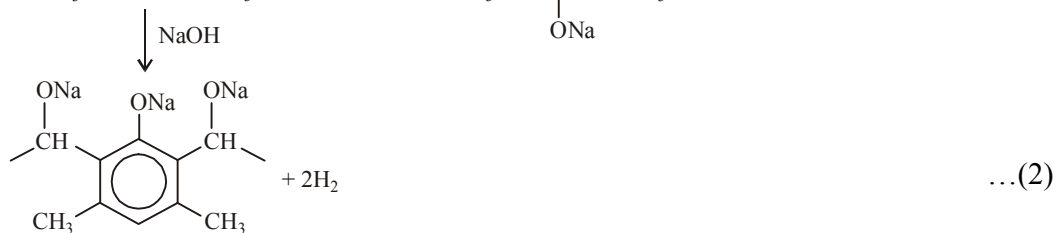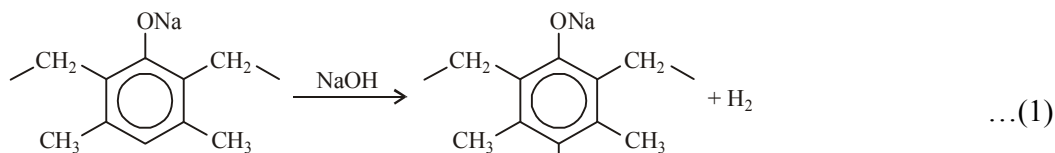$$\ldots(1)$$

$$\ldots(2)$$

$$\ldots(3)$$

Table 6 summarizes the data on low temperature Gray-king assay yield /100 g of overall coal/lignite, and per 100 g of Vitrinite of Dakra Bukbuka coal and Mahuda coal. It can be observed from the table that the tar /liquor, gaseous products and ammonia yields are invariably higher in Vitrinite than in overall coal, because Vitrinite is more reactive than other macerals like inertinite etc. When the coke yields are observed, it was found that in case of Mahuda coal, Vitrinite of Mahuda coal gave sharply better yield of coke than the overall Mahuda coal while the Vitrinite of Dakra Bukbuka coal yielded less coke than of its overall sample. This may be because the Dakra Bukbuka coal is semi-bituminous coal while the maturity of Mahuda coal, which is a coking coal, is higher. The mechanism of hydrogen formation can be explained as follows and shown in reactions (1) and (2). The hydrogen from hydroaromatic/aromatic part of the coal interacts with hydrogen of sodium hydroxide to form hydrogen gas. The –one group is now attached to the coal, which further reacts with hydrogen of aromatic/ hydroaromatic part forming fused rings and eliminating sodium hydroxide shown in reaction (3). In pyrolysis without using NaOH, maximum methane evolution occurred at about 480 and 560^0C, which corresponds to the decomposition of methyl groups and of the methylene groups, respectively[6,7]. In case of increasing NaOH, the reaction temperature shifted to a lower temperature. By addition of NaOH, the above reaction altered as shown in equations (1) and (2). The addition of NaOH causes the reaction and makes it difficult for the methylene groups to decompose into methane. The increase in the amount of methane with the addition of NaOH is the result of decrease in the tarry products. This decrease in tarry substances probably results from the rapid formation of dense network structure as illustrated in equations (1) and (2). The methane and hydrogen

evolved during the course of demethylation and dehydrogenation reactions in aromatic ring coalescence, respectively. The mechanism of the pyrolytic reaction changes in the presence of alkalies in such a way that CO_2/CO are absorbed, unsaturated hydrocarbon gets saturated by addition of hydrogen followed by cracking to yield hydrogen and methane, as also the tar formed hydrocracks to yield hydrogen and methane.

Table 6: LTGK Assay yield /100 g of overall and vitrain of coal/lignite

LTGK yield/100 g of dry coal/lignite	Neyveli		Dakra-Bukbuka		Mahuda	
	Overall	**Vitrain**	**Overall**	**Vitrain**	**Overall**	**Vitrain**
Coke in (g)	60.91	----	74.28	73.65	76.16	76.61
Tar (g)	13.99	----	12.64	10.37	14.98	12.63
Liquor (g)	3.71.	----	4.23	5.62	0.93	1.80
Gas (mL)	14912	----	8362	1041	7580	7774
Ammonia	0.08	----	0.10	0.13	0.08	0.09
Coke type	----	----	----	----	G-7	G-7

Table 7 presents the data on proximate and ultimate analysis of washed coal- char obtained from coal alkali interaction. The fifty percent of total hydrogen reduced during reaction in Dakra Bukbuka and Jeypore coal, but drastic change took place in Swang and Mahuda coals as well as Neyveli lignite. The total hydrogen available in char, which was obtained from coal-pyrolysis at 600^0C, is aromatic in nature. In this way, the generated data favors the participation of aromatic and hydroaromatic hydrogen of coal/ lignite for generating as a clean fuel hydrogen, by coal-alkali interaction.

Table 7: Proximate and Ultimate analysis of washed coal chars obtained from coal-alkali interaction at 600^0C

Coals	Proximate (dmf)				Ultimate (dmf)				
	%M	**%A**	**% VM**	**% FC**	**% C**	**% H**	**%N**	**%S**	**% O**
Neyveli	18.9	8.7	25.6	74.4	86.0	1.2	0.5	0.5	11.8
Dakra- Bukbuka	15.0	16.3	38.4	61.6	88.4	2.5	0.8	0.2	7.8
Jeypore	16.0	19.0	18.4	81.6	91.0	2.4	0.9	1.2	4.5
Swang	8.5	22.1	13.5	87.5	88.6	2.0	0.7	0.3	8.4
Mahuda	9.9	24.7	29.0	71.0	94.0	1.0	1.1	0.7	3.2

CONCLUSION

It is concluded that the optimum conditions for coal-alkali reaction is coal : alkali ratio is 1 : 1.33, temperature 600^0C, and most suitable alkali is NaOH, which produces only H_2 and CH_4 500 m^3 per ton and 75 m^3 per ton of coal, respectively. Japanese workers reported a similar yield but their heating rate was 3^0C/minute and temperature was 1000^0C, which is much higher than that in the present work. It is also pointed out in this work that the medium rank of coal with carbon (C 83-84%) is suitable for hydrogen production during pyrolytic condition and functional groups like -OH group, which plays an important role in hydrogen production. Higher the content of hydroxyl group, minimum is the hydrogen production. Hydrogen comes from dehydrogenation and demethylation of coal besides coalescence of aromatic rings. It is not necessary that coal having higher hydrogen can give more hydrogen, but that should also have aromaticity up to a certain level, as cited in this paper.

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