Alkali Carbonate and Nickel Catalysis of Coal Steam Gasification

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Introduction

Considerable work has been carried out on the catalytic effects of various chemicals on the reactions of carbon with with steam. This work is of classic importance in the water gas reactions. In addition, many studies have been made to determine active catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen. These two reaction systems are usually carried out at vastly different temperatures.

The carbon-steam reactions represented as $C + H_2O = CO + H_2$ and $C + 2H_2O = CO_2 + 2H_2$ are endothermic, and even in the presence of catalysts the operating temperature range of 800-1100°C is usually employed (1). One of the earliest investigations of catalysts for the carbon-steam reactions carried out by Taylor and Neville (2) was at temperatures from 490-570°C. Their most effective catalyst used with steam and coconut charcoal was potassium carbonate, although sodium carbonate also proved effective. Fox and White (2) demonstrated the catalytic effect of impregnating graphite with sodium carbonate over the temperature range of 750-1000°C.

Kröger (3) found that metallic oxides and alkali carbonates or mixtures catalyzed the carbon-steam reactions. Lewis and co-workers (4) stated that if reactive carbons are catalyzed with alkali carbonates reasonable gasification rates are attainable at temperatures as low as 1200°F. A process which uses molten sodium carbonate to catalyze as well as supply heat for the carbon-steam gasification, has been described (5).

In contrast to the carbon-steam reactions, the synthesis of hydrocarbons from carbon monoxide and hydrogen is usually carried out at temperatures below 450°C (6). The most active catalysts were found to be group VIII metals, mixed with various activating materials (7). A method for the direct production of hydrocarbons from coal-steam systems using multiple catalysts in a single-stage reactor has been described by Hoffman (8). Hoffman and co-workers (9) have described the effects of various commercial nickel methanation catalysts in a single-stage reactor. They stated that nickel was chosen for the methanation catalyst since the yield of hydrocarbons was limited essentially to methane.

It has been found in the single-stage reactor that most effective mixed catalysts which produce methane and carbon dioxide from coal-steam systems ($2C + 2H_2O = CH_4 + CO_2$) are potassium carbonate and nickel. In the single-stage reactor with the nickel methanation catalyst, potassium carbonate and coal mixed and charged, it is necessary in order to get effective contact time, to have the coal to nickel catalyst ratio about 1:1. With this in mind it was deemed significant to determine the optimum ratio of potassium carbonate to coal which would give the best methane production.

The principal objectives of this investigation were (1) to determine the optimum ratio of potassium carbonate to coal, holding the nickel catalyst concentration constant, (2) to determine by analytical methods and X-ray diffraction the form and recoverability of the potassium carbonate in the ash, and (3) to determine the amount of potassium that could be recovered economically.

Experimental Systems

Reactor Design: The gasification of coal was carried out in a one-inch (o.d.) diameter, semi-continuous flow reactor described in earlier papers (8,9). Due to the extremely active nature of the nickel catalyst towards oxygen, the re-reduced nickel catalyst had to be stored under nitrogen atmosphere. In addition, the reactor was charged under a nitrogen atmosphere in a glove box.

Feed Materials: The coal used in all runs was a sub-bituminous coal from Glenrock, Wyoming, ground to 60-100 mesh. An analysis of the coal is given in Table I. Certified A.C.S. anhydrous potassium carbonate was used for the alkali catalyst. This catalyst was approximately the same mesh size as the coal. X-ray studies indicate, however, that some of the potassium carbonate had become hydrated, for example $K_2CO_3 \cdot X(H_2O)$. In addition, a commercial nickel catalyst was employed. The nickel methanation catalyst (Ni-3210) containing approximately 35% by weight nickel on a proprietary support was purchased from the Harshaw Chemical Company. The nickel catalyst was reduced with H_2 at approximately 650°C for 12-18 hours and stored under a nitrogen atmosphere.

Table I. Analysis of Glenrock Coal

	Proximate Analysis	
	As Received	Moisture Free
Moisture (wt %)	12.2	----
Volatile Matter (wt %)	39.6	45.1
Fixed Carbon (wt %)	36.1	41.1
Ash (wt %)	12.1	13.8
Heating Value (Btu/lb)	9140	10410

	Ultimate Analysis	
	As Received	Moisture Free
Hydrogen (wt %)	5.1	4.3
Carbon (wt %)	52.7	60.0
Nitrogen (wt %)	0.6	0.7
Oxygen (wt %)	28.6	20.2
Sulfur (wt %)	0.8	1.0
Ash (wt %)	12.1	13.8

Gas Analysis: Product gas volumes were measured by a calibrated wet test meter. Gas compositions were determined with a Beckman Model GC-5 dual column, dual T.C.D. chromatograph. One detector used a helium carrier with

Pora-Pak Q column and other used an argon carrier with a molecular sieve column. Data reduction was aided by an Auto Lab System IV digital integrator equipped with a calculation module.

Analytical Analyses: The potassium remaining in the coal ash was determined with a Perkin-Elmer model 303 atomic absorption spectrophometer after performing a J. Lawrence Smith ignition on the sample. In order to obtain a total potassium balance it was necessary to recover the potassium that adhered to the nickel catalyst. This was accomplished by digesting the catalyst with acid and determining the potassium by atomic absorption.

The amount of carbonate retained in the ash was calculated from the quantity of carbon dioxide absorbed by ascarite after first scrubbing the gas evolved from the treatment of the ash with a 1:1 hydrochloric acid solution.

In order to determine the amount of potassium that was recoverable by an ambient temperature wash, 1g of ash was washed in 100ml of water for one hour. The amount of potassium in the filtrate was determined by atomic absorption.

X-ray Diffraction: The ground ash was mounted vertically in a General Electric XRD-5 diffractometer. Copper radiation at 50 KVP and 35 MA was used for the analyses. Each scan was started at an angle 2θ of 4° and continued through 70°. The "d" values in angstroms for the recorded X-ray peaks were determined from a copper $K\alpha$ (λ = 1.5418Å) table and compounds were identified from the A.S.T.M. X-ray Powder Data File.

Methodology: Experiments were carried out by charging the reactor with the coal, potassium carbonate and nickel catalyst mixture in a glove box under a nitrogen atmosphere. In those cases where no nickel catalyst was involved the reactor was not charged in the glove box. In all other runs 100g of coal and about 110g nickel catalyst with varying amounts of potassium carbonate were charged. The temperatures on the reactor and super heater were then brought to operating temperatures of approximately 650°C in less than two hours and maintained at the value for the duration of the run. In all cases the length of the run was 7 $^1/_2$ hours and approximately 28 ml of water were added. The product gas was monitored for composition every half hour. The reactor pressure was approximately 30 PSIA which in the pressure required to give an adequate sample to the chromatograph.

All runs were repeated until near duplication of two runs was obtained. The criteria for accepting the duplicate runs were based on the total mass balance and the quality of the gas produced. It was decided that a total mass balance of ±4% was sufficient to insure that there were no major leaks to prejudice the results. To insure that the nickel catalyst was properly reduced and had not oxidized during loading in the mixed catalyst runs, only the runs in which the average gas had a heating value of over 800 Btu/SCF (CO_2 free) were used. There were only two cases out of a total of twelve separate runs with the mixed catalyst where the quality of the gas produced was below 800 Btu/SCF. In both cases the runs were repeated a third time and the criteria for acceptance was met. The amounts of methane and gas produced per gram of coal reported in Table II are volume rated average compositions.

Results and Discussion

Table II contains a summary of the runs selected to determine the optimum amount of potassium carbonate to be mixed with the coal and nickel catalyst. Observations obtained with the single-stage reactor indicate that the initial reaction involved is devolatilization of the coal, followed by cracking and hydrogenation of unsaturated compounds in the presence of the nickel catalyst. This is followed by the carbon-steam reaction.

The first run in Table II was made using only coal and steam, and in this run the gas contained about 0.5% ethylene, 0.7% ethane as well as 4 ml of heavy liquids. In all the remaining runs the nickel catalyst was present, and in no case was any hydrocarbon heavier than methane detected. Methane and carbon dioxide were the major components, with hydrogen averaging between 10-14% and the carbon monoxide usually below 2.0% in the product gas. In run No. 2 only the nickel catalyst was employed. It more than tripled the methane production,while it only increased the total gas product by about 20%. This tends to indicate that a substantial quanity of the methane produced is derived from cracking and hydrogenating unsaturated compounds.

Figure 1 shows a plot of total gas production, as well as the methane production versus mass of potassium carbonate charged per 100g of coal. In both cases the dashed line indicates the runs were neither alkali or nickel

Table II Experimental Data for the Gasification Runs *

Run Number	1	2	3	4	5	6	7
K_2CO_3(g)	0.	0.	15.	20.	30.	45.	60.
Ni-3210(g)	0.	115.	111.	111.	111.	113.	114.
cm^3CH_4/g Coal	51.	185.	225.	281.	266.	232.	234.
cm^3Gas/g Coal	382.	453.	481.	612.	603.	493.	524.
Total Mass Recovery (wt %)	103.1	97.9	98.9	103.0	98.9	96.0	97.9
Total K Recovery (wt %)	____	____	94.2	105.7	105.9	95.0	98.7
K Recovery by Wash (wt %)	____	____	66.2	79.9	85.8	89.0	90.0
K Insoluble in Wash (g)	____	____	2.9	2.3	2.4	2.8	3.4
CO_3 Recovery (%)	____	____	97.7	101.2	104.1	101.8	104.8

*All runs were made at ~30 PSIA and an average temperature of ~650°C.

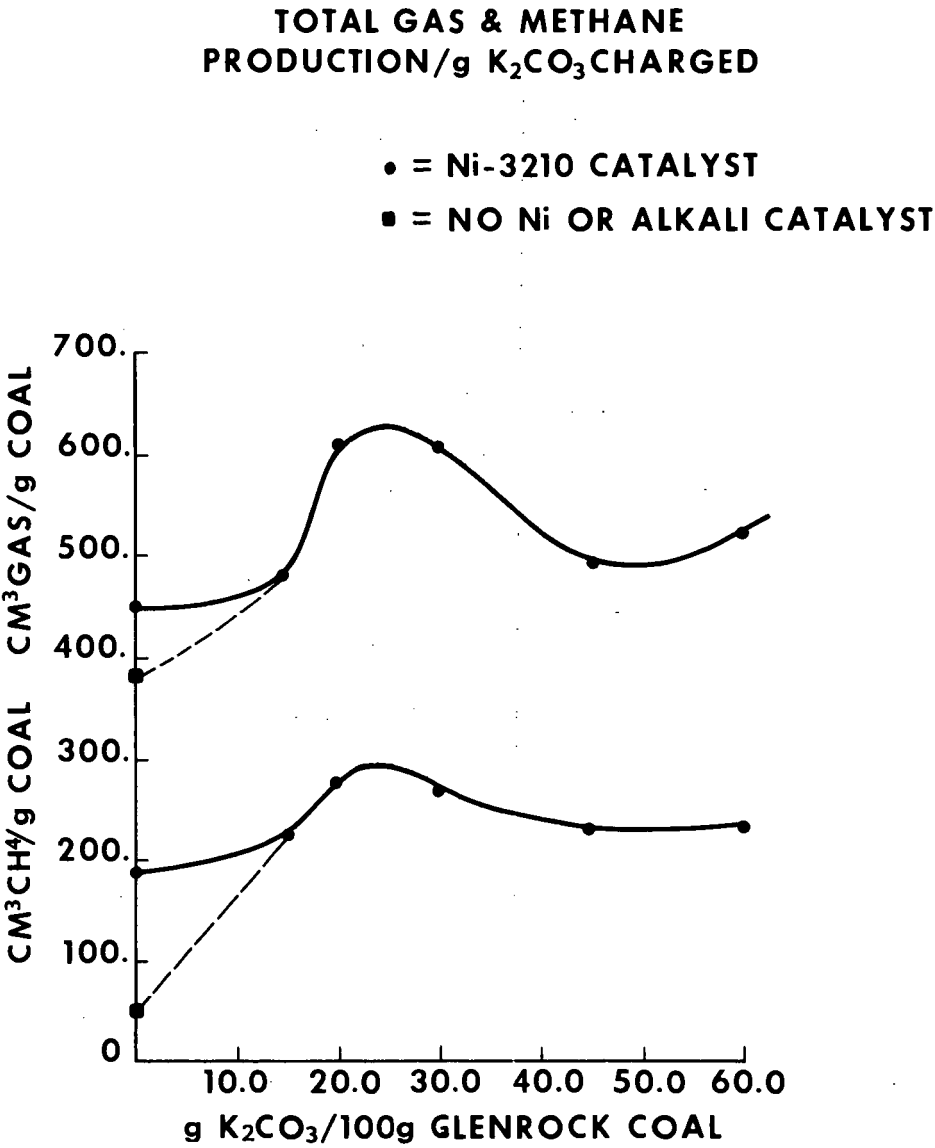
TOTAL GAS & METHANE
PRODUCTION/g K_2CO_3 CHARGED
• = Ni-3210 CATALYST
▪ = NO Ni OR ALKALI CATALYST
700.
600.
500.
400.
300.
200.
100.
0
CM^3CH^4/g COAL
CM^3GAS/g COAL
10.0
20.0
30.0
40.0
50.0
60.0
g K_2CO_3/100g GLENROCK COAL

Fig. 1

catalyst were present. These figures show that for the single-stage reactor, using a sub-bituminous coal at about 650°C, the optimum methane as well as gas production is obtained using between 20-25g of potassium carbonate per 100g of coal. Addition of more than 30g of potassium carbonate is detrimental to the methane production as well as total gas production. This decrease in production is readily apparant when the potassium carbonate has been increased to 45g.

Table II also contains the analytical results for potassium recovery and carbonate recovery. The total potassium recovery by the ignition method was satisfactory, giving deviations of ±6%. Potassium recovered in the wash solution varied from about 66 to 90%. This shows that between 2.3 - 3.4g of potassium are forming compounds that are insoluble in water at ambient temperatures. It is of interest to note that the least amount of insoluble potassium was obtained when the optimum amount of potassium carbonate was used. The carbonate recovered from the ash was good, giving a deviation of only ±5%.

Although the X-ray scan ran from an angle 2θ of 4-70°, the majority of the peaks of interest fell in the range of 20-44°. Table III compares "d" spacings and intensities of X-ray diffraction peaks from 20-44° 2θ for the published data on the hydrated potassium carbonate ($K_2CO_3.1\frac{1}{2}H_2O$) and silicon dioxide, with the potassium carbonate as received and the ashes from the runs containing 0, 20, 45, and 60g of potassium carbonate respectively. The "d" spacings and intensities of the potassium carbonate as received and of the ashes containing potassium carbonate do not correspond exactly to the published anhydrous or hydrated forms of potassium carbonate. For example, the published A.S.T.M. data shows the major peak for $K_2CO_3.1\frac{1}{2}H_2O$ (intensity 100) has a "d" spacing of 2.72Å, whereas the analyzed samples have major peak "d" spacings of 2.77Å for the ashes and 2.79Å for the potassium carbonate as received. It is believed that the analyzed form of the potassium carbonate as well as that in the ash is a partially hydrated compound.

Figure 2 shows the X-ray diffraction pattern for the potassium carbonate as received. Only the peaks with question marks are unidentified peaks. The peaks unlabelled correspond most nearly to those published for $K_2CO_3.1\frac{1}{2}H_2O$. The ash from the reactor run containing no potassium carbonate is shown in figure 3. It displays only silicon dioxide and some unidentified peaks. The ashes from runs using 20, 45, and 60g of potassium carbonate with 100g

Table III. Comparison of d Spacings and Relative Intensities for X-ray Diffraction Peaks from 20°-44° 2θ

$K_2CO_3 \cdot 1\frac{1}{2}(H_2O)$ ASTM 11-655		SiO_2 ASTM 5-0490		K_2CO_3 as received observed values			Ash with no K_2CO_3 observed values			Ash from 20g K_2CO_3 Run observed values			Ash from 45g K_2CO_3 Run observed values			Ash from 60g K_2CO_3 Run observed values		
				$K_2CO_3 \cdot x(H_2O)$		unidentified	SiO_2		unidentified	$K_2CO_3 \cdot x(H_2O)$		unidentified	$K_2CO_3 \cdot x(H_2O)$		unidentified	$K_2CO_3 \cdot x(H_2O)$		unidentified
d(1)	I/I_1(2)	d	I/I_1	d	I/I_1	d	d	I/I_1	d	d	I/I_1	d	d	I/I_1	d	d	I/I_1	d
-----	---	4.26	35	----	---	----	4.26	24	----	----	---	----	----	---	4.25	----	---	----
3.86	5	----	---	3.86	9	----	----	---	----	----	---	----	----	---	----	----	---	----
-----	---	----	----	----	---	----	----	---	----	----	---	3.71	----	---	----	----	---	----
-----	---	----	----	----	---	----	----	---	3.51	----	---	----	----	---	----	----	---	----
3.46	20	----	---	3.45	16	----	----	---	----	3.45	39	----	3.45	29	----	----	---	----
3.35	7	----	---	3.40	16	----	----	---	----	3.35	61	----	3.34	24	----	3.34	28	----
-----	---	3.343	100	----	---	----	3.35	100	----	----	---	----	----	---	----	----	---	----
3.31	20	----	---	3.30	11	----	----	---	----	3.30	48	----	----	---	----	----	---	----
-----	---	----	---	----	---	----	----	---	----	----	---	3.19	----	---	----	----	---	----
3.15	3	----	---	----	---	----	----	---	----	----	---	----	3.12	38	----	3.13	22	----
----	---	----	---	----	---	----	----	---	----	----	---	3.10	----	---	----	----	---	----
3.01	30	----	---	3.00	40	----	----	---	----	3.01	71	----	3.01	50	----	3.01	43	----
3.00	30	----	----	2.98	32	----	----	---	----	----	---	----	----	---	----	----	---	----
2.906	20	----	---	2.90	7	----	----	---	----	2.90	91	----	2.90	48	----	2.90	32	----
2.783	65	----	---	2.83	50	----	----	---	----	2.83	71	----	2.82	73	----	2.82	41	----
2.767	75	----	---	2.79	100	----	----	---	----	2.77	100	----	2.77	100	----	2.77	100	----
2.742	100	----	---	2.75	65	----	----	---	----	2.74	86	----	2.75	80	----	2.75	88	----
-----	---	----	---	----	---	2.62	----	---	----	----	---	2.63	----	---	2.629	----	---	2.63
-----	---	----	---	----	---	----	----	---	2.57	----	---	----	----	---	----	----	---	----
2.550	15	----	---	2.54	8	----	----	---	----	----	---	----	----	---	----	2.54	12	----
-----	---	----	---	----	---	----	----	---	----	----	---	2.49	----	---	----	----	---	----
-----	---	2.458	12	----	---	----	2.46	14	----	----	---	----	----	---	----	----	---	----
-----	---	----	---	----	---	2.38	----	---	----	----	---	----	----	---	----	----	---	----
-----	---	----	---	----	---	----	----	---	----	----	---	2.36	----	---	----	----	---	----
2.327	25	----	---	2.33	23	----	----	---	----	2.32	34	----	2.32 B	20	----	2.33	28	----
2.304	11	----	---	2.30	26	----	----	---	----	----	---	----	----	---	----	2.31	24	----
-----	---	2.282	12	----	---	----	----	---	----	----	---	----	----	---	----	----	---	----
2.267	15	----	---	----	---	----	----	---	----	----	---	----	2.26	18	----	2.26	18	----
2.259	15	----	---	2.26	17	----	----	---	----	----	---	----	----	---	----	----	---	----
-----	---	2.237	6	----	---	----	----	---	----	----	---	----	----	---	----	----	---	----
2.228	15	----	---	2.23	12	----	----	---	----	----	---	----	----	---	----	2.23	15	----
2.183	40	----	---	2.18	23	----	----	---	----	----	---	----	2.18	19	----	2.18	27	----
-----	---	----	---	----	---	----	----	---	----	----	---	2.16	----	---	----	----	---	----
-----	---	2.128	9	----	---	----	----	---	----	----	---	----	----	---	----	----	---	----
-----	---	----	---	----	---	2.11	----	---	----	----	---	----	----	---	----	----	---	2.11
-----	---	----	---	----	---	----	----	---	----	----	---	2.08	----	---	----	----	---	----

(1) Interplanar spacings

(2) Relative intensities

X-RAY DIFFRACTION PATTERN OF K_2CO_3 AS RECEIVED

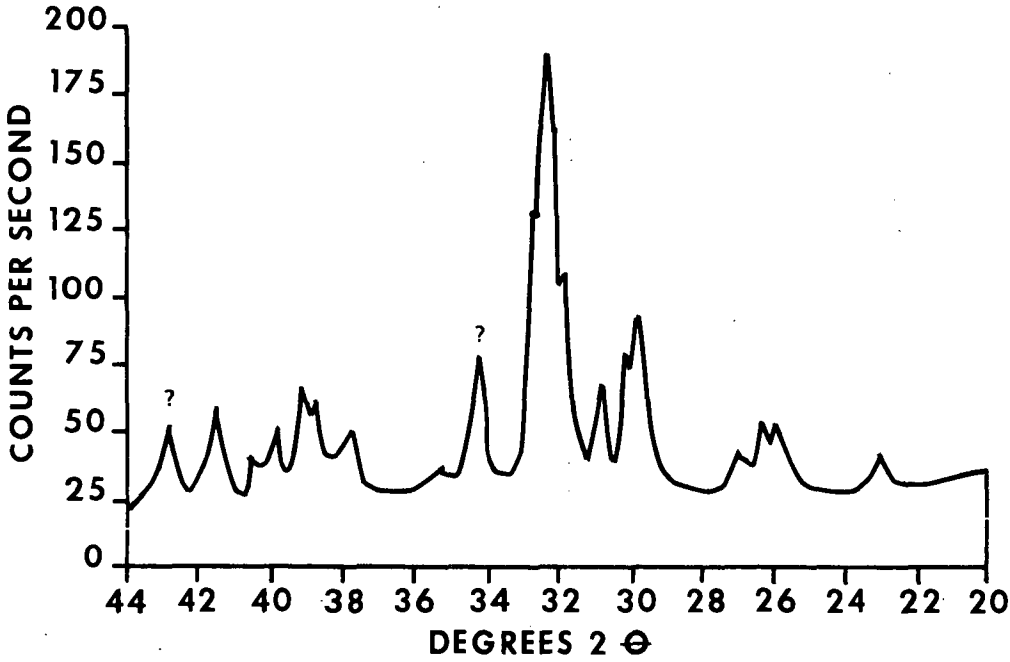

Fig. 2

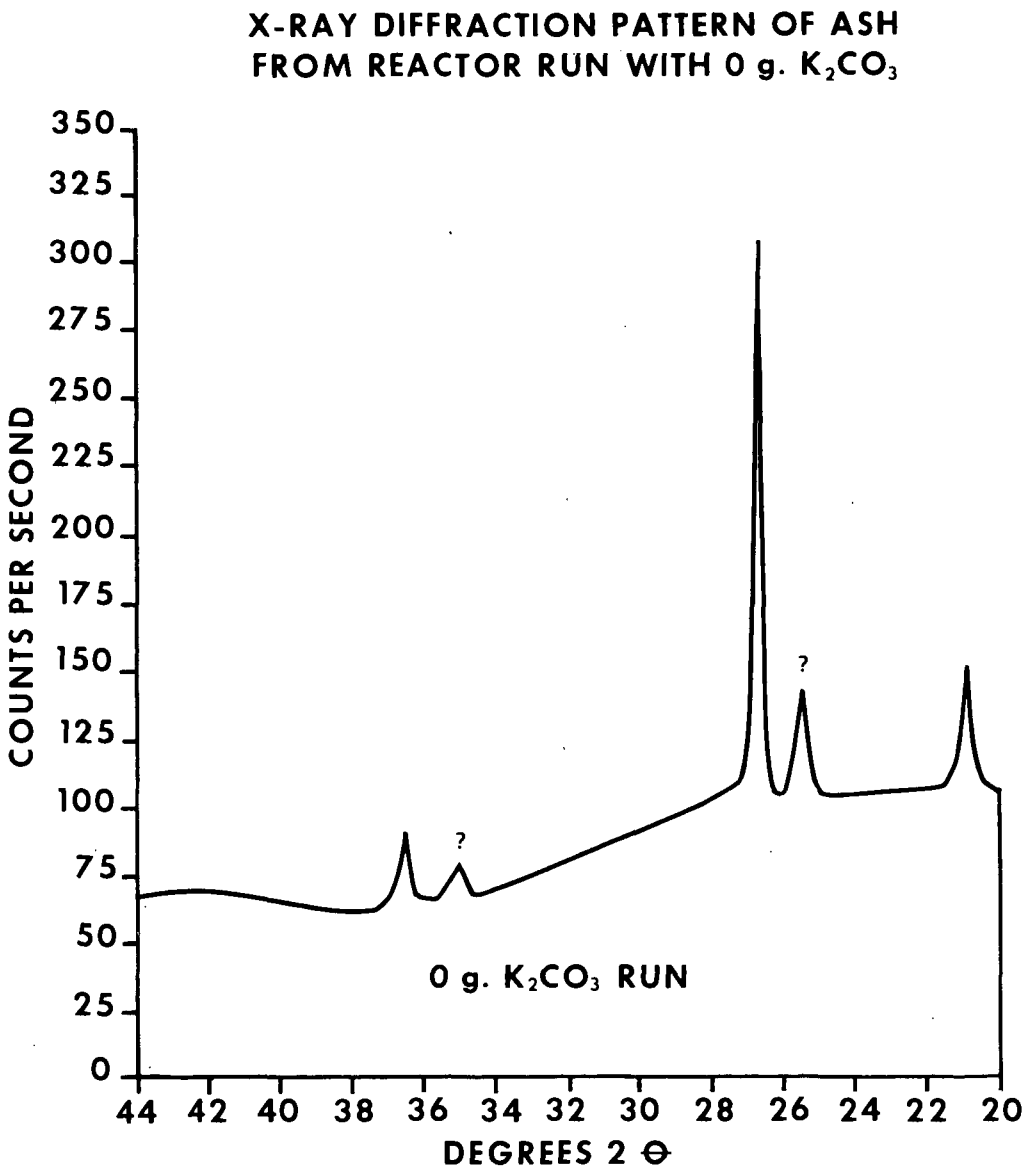
X-RAY DIFFRACTION PATTERN OF ASH
FROM REACTOR RUN WITH 0 g. K_2CO_3
COUNTS PER SECOND
350
325
300
275
250
225
200
175
150
125
100
75
50
25
0
?
?
0 g. K_2CO_3 RUN
44 42 40 38 36 34 32 30 28 26 24 22 20
DEGREES 2 Θ

Fig. 3

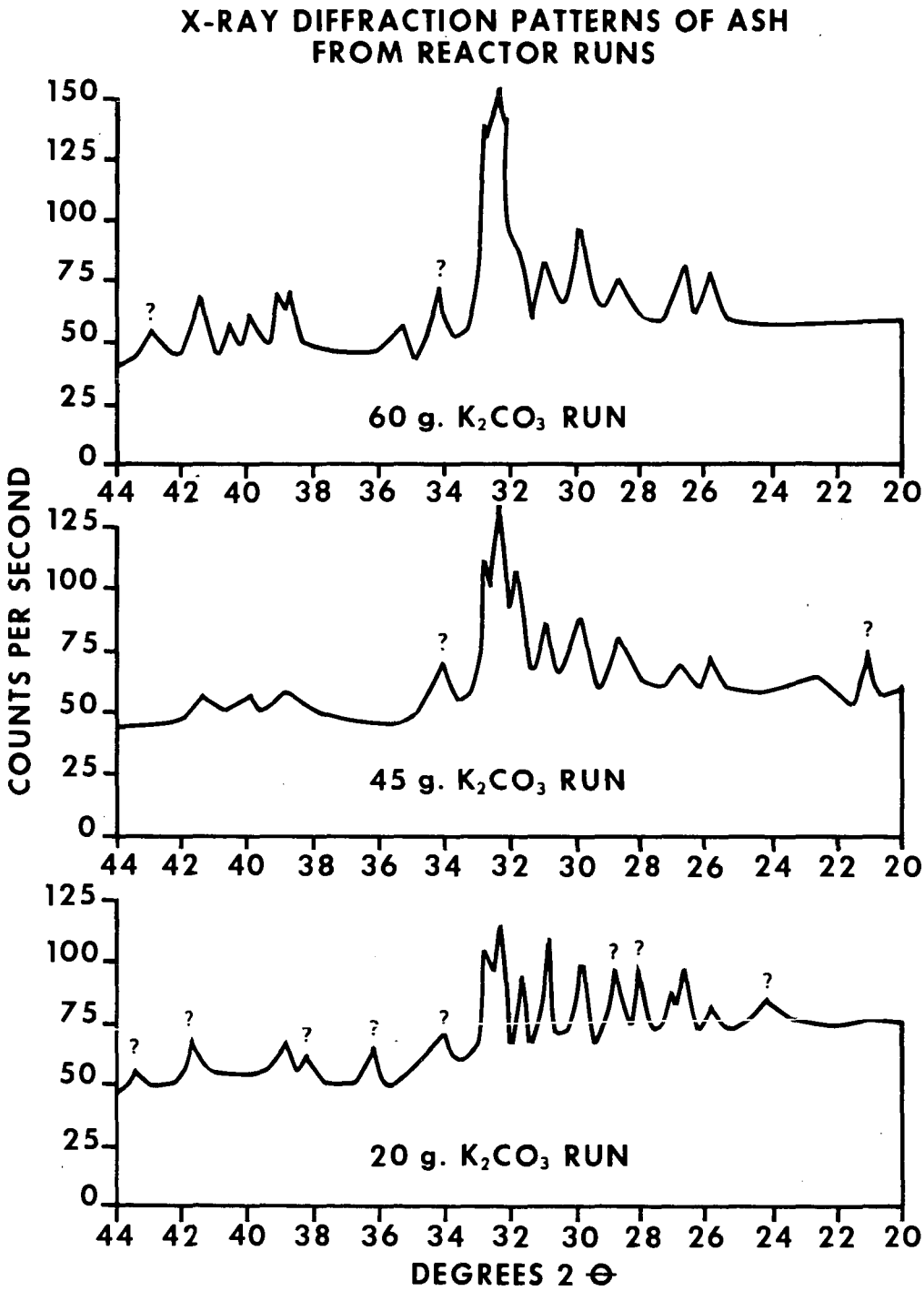
X-RAY DIFFRACTION PATTERNS OF ASH
FROM REACTOR RUNS
COUNTS PER SECOND
60 g. K_2CO_3 RUN
45 g. K_2CO_3 RUN
20 g. K_2CO_3 RUN
DEGREES 2 θ

 Fig. 4

of coal charged are shown in figure 4. It indicates that the amount of potassium carbonate remaining in the ash is proportional to the amount charged. This is best observed by noting the changes in the intensities of the major potassium carbonate peaks between 32-33° 2θ. Again the peaks that are unidentified are noted with question marks. Comparison of "d" values in table II indicate that the form of the potassium carbonate remains essentially unchanged after the reaction.

Conclusions

The investigations thus far indicate that it is possible in a single-stage reactor, by using a mixed catalyst of potassium carbonate and a nickel catalyst, to react coal and steam principally to methane and carbon dioxide at low pressure and temperatures of approximately 650°C. Under these conditions the optimum amount of potassium carbonate for maximum methane production is between 20-25% the mass of the coal. X-ray diffraction studies indicate that the form of the potassium carbonate remaining in the ash is essentially the same as that charged. At the observed optimum value of 20g of potassium carbonate to 100g of coal nearly 80% of the potassium is recoverable by a one hour wash with water at room temperature.

Selected References

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