Journal of Engineering Science 08(1), 2017, 11-16

JES
an international Journal

PRODUCTION OF CARBON-DI-SULPHIDE BY REACTION OF BY-PRODUCT GYPSUM WITH CARBON TETRACHLORIDE VAPOUR

Nurul Hoque Bhuiyan[1], Matiur Rahman[1] and Samarendra Karmakar[1,2]

[1]*Bose Centre for Advanced Study and Research, Department of Applied Chemistry*
Dhaka University, Bangladesh
[2]*Bangladesh centre for Advanced Studies, Dhaka, Bangladesh*

Received: 12 September 2016 Accepted: 11 June 2017

ABSTRACT

Reaction between by-product gypsum and carbon tetra chloride vapour in presence of activated charcoal has been studied. The effects of temperature, time and the amounts of the reactants on the percentage yield of the products have been shown. It was observed that under optimum conditions 98.32% carbon-di-sulphide and 93.49% calcium chloride were obtained at 800℃ within two hours. The process may be utilized as a useful method for the production of a valuable solvent like carbon-di-sulphide.

1. INTRODUCTION

The world deposit of sulphur is being reported to be exhausted day by day. Our country does not have any sulphur deposit in any form. The disposal of the huge amount of gypsum, a waste product of the TSP Factory at Chittagong, is a major problem for that industry. The feasibility study of the utilization of this gypsum particularly for converting its sulphur content into a useful product will be a very interesting work. Information on the recovery of the sulphur component of gypsum is very scanty. So far the work on the utilization of gypsum has been limited to its reduction to sulphide by hydrogen (Unger and Liebigs, 1848), carbon (Pechvoskii *et al.* 1960; Kunhein, 1900) , water-gas, methane (Bobrovnik *et al.*, 1964) etc. and chlorination by hydrogen chloride to anhydrous metal chloride (Mantrand, 1954). Most recently a work on the preparation of carbon-di-sulphide from A.R. calcium sulphate has been reported with encouraging results (Bhuiyan and Rahman, 1976). So the present reaction of by-product gypsum with carbon tetra-chloride vapour in presence of active charcoal was taken up for detailed investigation.

Thermodynamic Consideration: The probable main reactions that are believed to take place in the process are:

$$CaSO_4 + 4C = CaS + 4\,CO \qquad (1)$$

$$CaS + \frac{1}{2}CCl_4 = CaCl_2 + \frac{1}{2}CS_2 \qquad (2)$$

Overall reaction: $CaSO_4 + 4C + \frac{1}{2}CCl_4 = 4\,CO + CaCl_2 + \frac{1}{2}CS_2$ **(3)**

The thermodynamic feasibility of the above reactions was calculated from the following equation:

$$\Delta G_T = \Delta H_{298} - T\Delta S_{298}$$

The computed values of ΔG_T for reactions (1), (2) and (3) were calculated and are given below (Bhuiyan and Rahman, 1976):

reaction (1): $\Delta G_T = (+124{,}110 - 166.36T)$ Cal

reaction (2): $\Delta G_T = (-\,51{,}525 - 5.144T)$ Cal

reaction (3): $\Delta G_T = (+\,72{,}585 - 171.5T)$ Cal

The ΔG_T values of reactions (1), (2) and (3) change respectively from +12,150 to -87,666 Cal, -54,987 to -58,073 Cal and -42,835 to -145,735 Cal over the temperature range of 400-1000°C.

Thus, it may be concluded that overall reaction is quite feasible and would be favoured at higher temperatures.

* Corresponding Author: karmakarsamarendra@gmail.com

2. EXPERIMANTAL

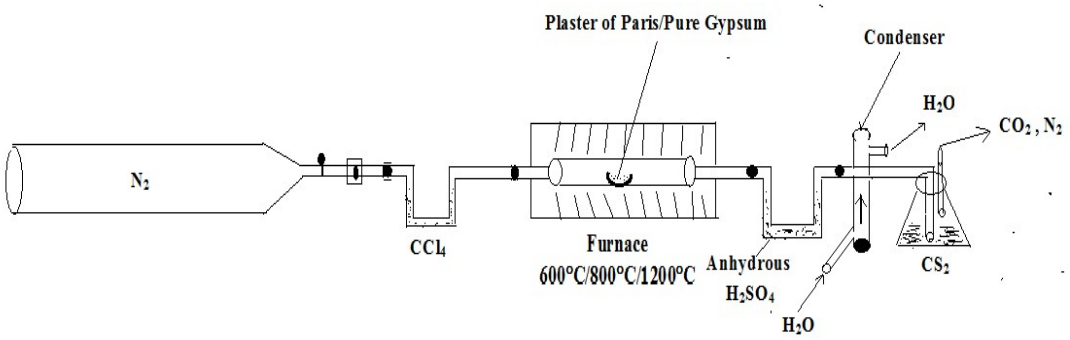
2.1 Purification of Gypsum

A sample of gypsum was treated with 100 ml of 0.5 M sulphuric acid solution. It was stirred thoroughly and the supernatant liquid was decanted off. The process was repeated for five times. The residue left was washed with distilled water repeatedly until it was free from acid. It was then treated with rectified spirit and finally dried at 110 °C in an electric oven for 2 hours. The gypsum was then converted to Plaster of Paris by heating the sample at 120-150 °C for 2 hours (Shreve, 1956). After analysis, Plaster of Paris was found to have a purity of 99.56%. All the reactions were carried out with this sample of gypsum thus purified.

2.2 Apparatus and Procedure

The experimental set up is shown in Figure 1. The solid reactants were put in a silica boat which was placed in a reaction tube. The reaction tube was then put inside a furnace in such a way that the reactants were at the central zone of the furnace. The temperature of the furnace was measure with a Pt/Pt-Rh thermocouple. The temperature of the furnace was controlled to within ±5 °C. Then dry nitrogen was passed through the system for some time. The temperature of the furnace was raised to the desired point and CCl_4-vapour from a specially designed. CCl_4-bubbler was delivered on to the silica boat through a ceramic feeding tube with the help of high pressure nitrogen as the inert carrier gas. The anhydrous $CaCl_2$ formed remained in the silica boat. The gaseous CS_2 evolved was absorbed in 5% alcoholic KOH solution (Vogel A. I., 1962).

Figure 1: Experimental set up



2.2.1 Feeding of CCl_4

Nitrogen gas was passed successively through a reservoir, a H_2SO_4-bubbler, a two-way stopcock and then through a specially designed bubbler containing CCl_4 whose temperature was raised to about 60 °C and kept there by intermittent heating. When nitrogen gas was thus passed at a pre-determined rate, it gave a certain rate of flow of CCl_4-vapour through the reaction tube.

2.2.2 The REACTION

A weighed amount of plaster of paris obtained from gypsum was mixed thoroughly with a definite amount of activated charcoal. A silica boat containing this mixture was kept at the entrance end of the reaction tube which in turn was put in an electric tube furnace. Pure nitrogen gas was passed straight through the system

for sometime. The temperature of the furnace was then raised to the desired point and was kept constant. The boat containing the reactants was pushed to the middle of the reaction tube and nitrogen gas was allowed to pass through the CCl_4-bubbler. The time of reaction was recorded from the moment CCl_4-vapour was first introduced into the system.

Observation: Traces of sulphur, hexachloro-ethane and sulphur chloride (if any) condensed at the cooler exit end of the reaction tube and sometimes dripped down the ground joints into the condenser flask. Carbon-di-sulphide passing over was absorbed in the flask containing alcoholic KOH solution. At the end of the reaction, the furnace was switched off and the whole system was cooled down to room temperature with a slow stream of nitrogen still flowing.

2.2.3 Analysis

The main reaction products were carbon-di-sulphide and calcium chloride. Calcium chloride remained in the boat with unreacted $CaSO_4$ and CS_2 was absorbed in the alcoholic KOH solution.
The solid residue was treated with warm water to dissolve out $CaCl_2$, which was subsequently determined by the estimation of chlorine titrimetrically and calcium as Ca-oxalate. No sulphide or sulphate was found to be present in the aqueous extract.
The CS_2 recovered as xanthate was determined by the method of Khundakar and Eusuf, 1961. The alcoholic KOH solution was found to be free from chloride and contained only xanthate.

3. RESULTS AND DISCUSSION

Several experiments were carried out to find out the effect of variation of temperature, time, CCL_4 input and active charcoal on the progress of the reaction. The results are shown in Tables 1-4.

3.1 Effect of Temperature

It was observed from the results of some preliminary experiments that a temperature below 700°C and above 900°C was not suitable for a reactionable yield of the products. A number of experiments were carried out between 700 and 900°C keeping the amount of reactants, duration and other experimental conditions constant. Results are depicted in Table 1.

Table 1: Effect of temperature on the progress of the reaction

$CaSO_4.\frac{1}{2}H_2O$ =2.0 g; Active charcoal=0.706 g; CCl_4 =1.8 ml; Duration =2.5 hours.

Temperature (°C)	Amount of $CaCl_2$ (g)	%yield of $CaCl_2$	% $CaSO_4.\frac{1}{2}H_2O$ Converted to $CaCl_2$	CS_2 recovered	
				As sulphur	As %throughput of sulphur
700	0.7800	50.65	51.00	0.0771	34.27
800	1.4200	92.25	92.75	0.2112	49.16
900	1.4240	92.50	93.01	0.1534	37.37

It is seen from Table 1 that the rise of temperature from 700°C to 800°C has increased the conversion of $CaSO_4.\frac{1}{2}H_2O$ to $CaCl_2$ from 51.00 to 92.75% and CS_2 recovered as percentage throughput of sulphur from 34.27 to 49.16. At higher temperature (900°C), however, the reaction does not seem to be more favourable as the CS_2 recovered has fallen considerably. The optimum temperature for these reactions was found to be

800°C. The table further shows that %yield of $CaCl_2$ is equal to % $CaSO_4.\frac{1}{2}H_2O$ converted to $CaCl_2$. This implies that variation is only due to calcinations.

3.2 Effect of Time

Experiments were carried out at 800 °C to find out the effect of duration of reaction on the yield. In these experiments only the duration of reactions was varied from 1 to 2.5 hours while the reactants and all other experimental conditions were kept identical. The results are given in Table 2.

It is observed from Table 2 that when the time of reaction was increased from 1 to 2 hours the conversion of $CaCl_2$ increased from 41.15% to 96.56% and the sulphur throughput recoverable as CS_2 increased from 28.14 to 67.64%. But when the time of reaction was extended up to 2.5 hours the yield in both cases slowed down. Maximum yield was obtained in experiment continued for 2 hours. So, this is the optimum time.

Table 2: Effect of time

$CaSO_4.\frac{1}{2}H_2O$ =2.0 g; Active charcoal=0.706 g; CCl_4 =1.8 ml; Temperature = 800°C

Time in hours.	Amount of $CaCl_2$ formed (g)	%yield of $CaCl_2$	% $CaSO_4.\frac{1}{2}H_2O$ converted to $CaCl_2$	CS_2 recovered	
				As sulphur (g)	As %throughput of sulphur
1.0	0.6300	40.90	41.15	0.0511	28.14
1.5	1.2230	79.41	79.88	0.1715	48.66
2.0	1.4783	96.00	96.56	0.2882	67.64
2.5	1.4200	92.25	92.75	0.2112	49.16

3.3 Effect of CCl_4

Experiments were carried out to study the effect of CCl_4 input in two hours. Here only the amount of CCl_4 input was varied from 1.573 to 4.002 g, while other variables were kept constant.

Table 3: Effect of CCl_4 input

$CaSO_4.\frac{1}{2}H_2O$ = 2.0 g; Active charcoal = 0.706 g; Temperature = 800°C; Time = 2.0 hours

CCl_4 input (g)	Flow rate of CCl_4 (g/hour)	Amount of $CaCl_2$ formed (g)	%yield of $CaCl_2$	% $CaSO_4.\frac{1}{2}H_2O$ converted to $CaCl_2$	CS_2 recovered	
					As sulphur (g)	As %throughput of sulphur
1.513	0.7565	1.4819	96.22	96.79	0.2100	49.18
2.882	1.4410	1.4783	96.00	96.56	0.2882	67.64
3.361	1.6805	1.4800	96.10	96.66	0.27984	65.61
4.002	2.0010	1.4140	92.00	92.49	0.1903	46.63

It is found from Table 3 that 2.882 g of CCl_4 was required for the highest conversion of the sulphur throughput to CS_2 while 96.56% of total $CaSO_4.\frac{1}{2}H_2O$ was converted to chloride. Further increase of CCl_4 input did not improve the CS_2 recovery.

3.4 Effect of active charcoal

To find out the effect of active charcoal, a number of experiments were carried out using 2.882g of CCl_4 input in each case. Amount of active charcoal was varied from 0.3 g to 1.0 g and the other variables were kept identical. Maximum conversion (98.32%) of sulphur throughput to CS_2 was obtained with 0.5 g of charcoal.

Table 4: Effect of active charcoal

$CaSO_4.\frac{1}{2}H_2O$ =2.0 g; CCl_4 =2.882 g; Temperature = 800°C; Time 2.0 hours

Amount of charcoal (g)	Amount of $CaCl_2$ formed (g)	%yield of $CaCl_2$	% $CaSO_4.\frac{1}{2}H_2O$ converted to $CaCl_2$	CS_2 recovered	
				As sulphur (g)	As %throughput of sulphur
0.3	1.400	90.91	91.44	0.2950	73.11
0.5	1.4400	93.49	94.06	0.4081	98.32
0.706	1.4783	96.00	96.56	0.2882	67.64

It is found from Table 4 that with the increase of the amount of charcoal from 0.3 to 0.5g, the percentage conversion of $CaSO_4.\frac{1}{2}H_2O$ converted to $CaCl_2$ and CS_2 recovered as %throughput of sulphur are found to increase. Further increase of the amount of active charcoal did not have any beneficial effect on the yield of carbon-di-sulphide.

Thus, it is found that when 2.0g of plaster of paris obtained from gypsum was mixed with 0.5g of active charcoal and was reacted with 2.882g of CCl_4-vapour at 800°C, 94. 06% $CaCl_2$ and 98.32% of CS_2 were obtained.

4. CONCLUSION

A method has been developed for the preparation of carbon-di-sulphide from by-product gypsum. Under optimum conditions, when CCl_4 is passed over plaster of paris obtained from gypsum in presence of active charcoal at 800°C, 94. 06% of anhydrous $CaCl_2$ and 98.32% of CS_2 are obtained.

ACKNOWLEDGEMENT

The authors acknowledge the financial help provided by the University of Dhaka and the University Grant's Commission of Bangladesh.

REFERENCES

Unger, B. and Liebigs, J. Am. Chem. Soc, (1848), Vol. 64, pp. 39.

Pechvoskii, V. V., Amirova, S. A. and Ketov, A. S., Uch. Zap Permsk. Gos. Univ., (1960), Vol. 17(1), pp. 3-14.

Kunhein, Veber die Einwir-Kung, des Licthogens and Gemischevon sulpaten mit Kohle, Berlin, (1900).

Bobrovnik, D. P., Vestn, L. and Vovsk. G., Univ., Ser. Geol. Russia, (1964), Vol. 2, pp. 3-8.

Mantrand, M. C., Compt, Rend., (1954), Vol. 38, pp. 846.

Bhuiyan, N. H. and Rahman. M., J. Appl. Chem. Biotechnol., (1976).

Shreve, R. N., The Chemical Process Industries, 2nd ed., McGraw-Hill Book Company, Inc., New York, (1956), p-218.

Vogel, A. I., A Text Book of Quantitative Inorganic Analysis, Longmans, Green and co. Ltd., London, 3rd Edn., (1962).

Khundakar, M. H. and Eusuf, M., Analytica Chem. Actd., (1961), Vol. 24, pp. 419.