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Studies of "Manganese Cycle" for Gasification of Solid Carbon Resources. I. Formation and Hydrolysis of Manganese Carbides and Their Repetition

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A new carbide method based on "Manganese Cycle" was studied in order to produce new fuel gas. This process consists of four steps; (i) carbide production from Mn_2O_3 and solid carbon sources, (ii) fuel gas production by means of hydrolysis of the carbide, (iii) spontaneous oxidation of $Mn(OH)_2$ with air to Mn_2O_3, and (iv) regeneration of the carbide from Mn_2O_3 and new carbon sources. In this process, manganese is used as a recyclable medium for gas production, and hydrogen and hydrocarbons (C_1–C_5) are obtained by hydrolysis. Carbon monoxide generated during the formation of the carbide is also utilizable. The addition of Li_2CO_3 was effective for the carbide reproduction.

Recently, much thought has been given to the development of new energy sources replaceable for fossil fuels. And also, many investigators have studied the effective utilization of coal or the other solid carbon sources, which have been wasted or poorly utilized. Production of salt-like carbides and their hydrolysis to obtain hydrocarbons is one of the prospective methods for the gasification of solid carbon sources. Although carbide technology for acetylene production was one of important chemical industries, very high temperature (>2000 °C) is necessary to produce calcium carbide and, nowadays, the technology is unprofitable for the production of organic raw materials. It is desirable to research other salt-like carbides which can be prepared at much lower temperatures.

Tamers[1,2] has proposed the process for total synthesis of benzene by using lithium carbide as the intermediator. His process consists of four steps; (1) production of Li_2C_2 (at 1000 °C), (2) hydrolysis of Li_2C_2 to produce C_2H_2, (3) regeneration of Li from its hydroxide or oxide, and (4) conversion of C_2H_2 to benzene.

Manganese carbides may be another candidate for such a recyclable fuel production medium. Mn_3C is produced at about 1000 °C and hydrolyzed at room temperature to evolve hydrogen and methane ($Mn_3C+6H_2O \rightarrow 3Mn(OH)_2+H_2+CH_4$).[3] The formation and stability of the manganese carbides have been studied by many workers.[4—10] Recently, Christopher[11] has proposed that iron–manganese carbides can be used to produce liquid hydrocarbons by the hydrolysis at high temperature. In his process, since iron(III) chrolide was used to promote the formation of iron–manganese carbide, the latter may be difficult to recycle. And the necessity of the repeated quenching process of the carbides (Mn_3C+Fe_3C) makes the process complicated.

We propose "Manganese Cycle" to produce new fuel gas. As shown in Fig. 1, this process consists of four steps:

(i) Carbide production from Mn (or oxides) and solid carbon sources.

$$x\,\mathrm{Mn} + y\,\mathrm{C} \longrightarrow \mathrm{Mn}_x\mathrm{C}_y \tag{1}$$

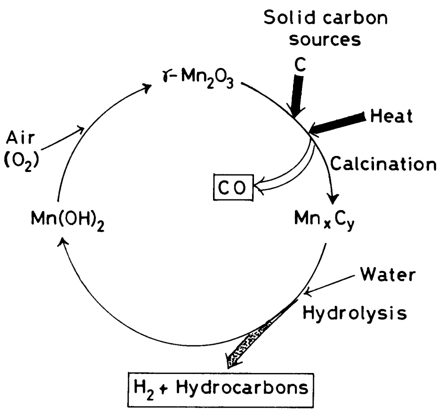

Fig. 1. Schematic illustration of "Manganese Cycle" for gasification of solid carbon resources.

or

$$x\,\mathrm{MnO}_z + (y+xz)\mathrm{C} \longrightarrow \mathrm{Mn}_x\mathrm{C}_y + xz\,\mathrm{CO} \tag{2}$$

(ii) Fuel gas production by means of the hydrolysis of the carbide.

$$\mathrm{Mn}_x\mathrm{C}_y + \mathrm{H_2O} \longrightarrow \mathrm{H_2} + \text{hydrocarbons} + x\,\mathrm{Mn(OH)_2} \tag{3}$$

(iii) Spontaneous oxidation of $Mn(OH)_2$ to Mn_2O_3.

(iv) Regeneration of the carbides from Mn_2O_3 and new carbon sources (the same process as Eq. 2).

Consequently, we can obtain hydrogen and hydrocarbons with hydrolysis of the carbides and, in addition, carbon monoxide during the production of the carbides. Since the manganese source can be recycled, we have only to charge the solid carbon sources and water to this process.

In the present study, we investigated this new carbide method with respect to the formation of manganese carbides, their hydrolysis for gas production and the recycle of manganese in the process.

Experimental

As the starting materials, manganese powder (purity 99.00—99.98%) and graphite powder were used. They were

Table 1. Formation of manganese carbides and the volume of gas evolved by hydrolysis at 50 °C

No.	Mn/C (charged)	Calcining Temperature/°C	Time/h	Produced carbide$^{a)}$	Gas volume$^{b)}$/cm^3 g^{-1}
1	1.5	800	15	◎ Mn_7C_3, △ Mn_5C_2	197.8
2	2.0	800	15	○ Mn_7C_3, ○ Mn_5C_2	206.4
3	2.5	800	15	○ Mn_5C_2, ○ $Mn_{23}C_6$	200.9
4	2.5	1000	3	◎ Mn_5C_2, ▲ Mn_3C	218.8
5	3.0	1000	3	○ $Mn_{15}C_4$, ○ Mn_5C_2, △ Mn_3C	172.6

a) Observed phase by X-ray diffraction: The symbols indicate the relative intensity (◎>○>△>▲). b) Volume of gas at 25 °C and 1 atm(101.3 kPa) evolved by hydrolysis.
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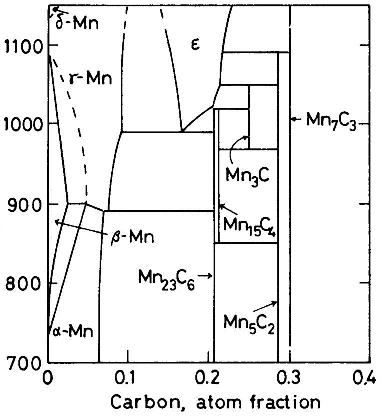

Fig. 2. Manganese–carbon phase diagram.7)

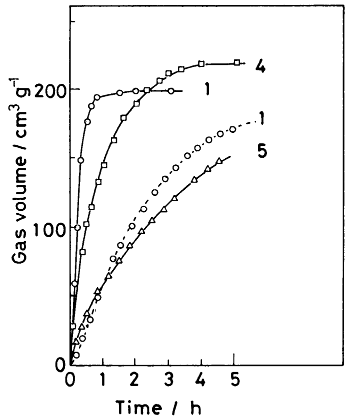

Fig. 3. The volume of evolved gas during hydrolysis. ---: Hydrolyzed at 50 °C, ---: hydrolyzed at 18 °C. (The volume of the gas is converted to a dry basis at 25 °C, and at 101.3 kPa, and the sample No. in the figure is same as in Table 1)

mixed and pressure molded at 400 kg cm^{-2} into the cylindrical form (dia; 14 mm). Test specimens were set in a ceramic tube and calcined at 500—1000 °C in vacuum (0.4—2.0 Torr†)) for 3—15 h. After the calcination, specimens were cooled by removing the ceramic tube from the furnace. The carbides thus obtained were identified by X-ray powder diffraction (Fe-*Kα*) and subjected to hydrolysis test.

The hydrolysis experiment was carried out by using a gas burette. Since $Mn(OH)_2$, the precipitate by hydrolysis, absorbs oxygen to form γ-Mn_2O_3, the gas burette was purged with dry nitrogen gas before the hydrolysis. The evolved gas was analyzed by gas chromatography (Yanagimoto, Rapid Gas Analyzer G-1001).

Results and Discussion

Formation of Carbides and Their Hydrolysis. The calcined products obtained by the above described method were the mixtures of carbides and carbon, the composition of which depended on the firing temperature and the ratio of the starting materials. Typical examples of the products are shown in Table 1. We obtained different kinds of carbide including Mn_5C_2, Mn_7C_3, $Mn_{15}C_4$, Mn_3C, and $Mn_{23}C_6$ by changing the ratio of Mn to C(Mn/C=1.5—3.0) in the starting material and the calcining temperature (500—1000 °C). Figure 2 shows the currently accepted manganese-carbon phase diagram.7) Our results exhibited almost mixed phase probably due to insufficient equilibrium time and a rather slow cooling rate.

Some workers have reported the hydrolysis of Mn_3C3,8), Mn_5C_2,8) and Mn_7C_3.10) However, the volume and the composition of the evolved gas were not so clear for some carbides. The volume of evolved gas during hydrolysis of our products (cm^3 per 1 g of the product, at 25 °C and 1 atm†)) is also shown in Table 1. Figure 3 shows the increase in the gas volume with time. These carbides could be hydrolyzed more rapidly at 50 °C than at room temperature. While the decomposition of the carbides containing $Mn_{15}C_4$ (calcined at 1000 °C) were rather slow, the hydrolysis of Mn_5C_2 and Mn_7C_3 took place very easily at 50 °C. A hard and dense sinter was observed in the case of No. 5 product. The maximum gas volume evolved was about 220 cm^3 g^{-1} for the product mainly composed of Mn_5C_2. After the hydrolysis, gray precipitate, whose X-ray diffraction gave a broad and weak lines corresponding to $Mn(OH)_2$, was observed in all cases. This precipitate changed gradually dark brown colored γ-Mn_2O_3 on exposure to air.

Compositions of the Gas Evolved. The composition of the product gases was analyzed by gas chromatography and results are shown in Table 2. The calcined product mainly composed of Mn_5C_2 (No. 4 in Table 1) evolved hydrogen, methane, ethane, propane and a small amount of ethylene. On the other hand, much more varieties of hydrocarbons could be detected

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† 1 Torr=133.322 Pa.

† 1 atm=101.3 KPa.

TABLE 2. COMPOSITION OF THE GAS EVOLVED BY HYDROLYSIS AT 50 °C

Carbide	Composition/%[a)]										
	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}	x	y	Mn/C[b)]
No. 1(Mn_7C_3 rich)	48.13	37.43	0.21	9.52	0.22	2.91	0.08	0.24	1.659	0.675	2.46
No. 4(Mn_5C_2 rich)	51.48	36.89	0.10	7.57	—	0.93	—	—	1.519	0.550	2.76

a) Residual gas (1—3%) is air. b) Ratio of Mn to C in the caribide calculated assuming Eq. 4.

in the case of No. 1 product mainly composed of Mn_7C_3. In this experiment, trace amount of C_5-hydrocarbons were sometimes detected. Such composition for our No. 1 product was in good agreement with that for Mn_7C_3 reported Hajek *et al.*[10)]

Kor[8)] has reported the composition of the evolved gas from the hydrolysis of Mn_5C_2 at 20 °C. His analysis by mass spectrometry found hydrogen, methane, ethane, and propane. And he has also reported that the ratio of Mn to C (Mn/C) calculated from the composition of the product is 2.4 or 2.7 for Mn_5C_2. Then we calculated the ratio of Mn to C by a similar way. The reaction equation of the hydrolysis of the carbide, Mn_xC_y, can be written as Eq. 4 assuming that the precipitate is only composed of $Mn(OH)_2$.[8)]

$$\begin{aligned}Mn_xC_y + a\,H_2O &\longrightarrow x\,Mn(OH)_2 + p\,H_2\\ &+ q\,CH_4 + r\,C_2H_4 + s\,C_2H_6 + t\,C_3H_6\\ &+ u\,C_3H_8 + v\,C_4H_8 + w\,C_4H_{10} \qquad (4)\end{aligned}$$

The values of x and y were calculated from the gas composition and results are shown in Table 2. Mn/C was 2.76 for the carbide mainly composed of Mn_5C_2 (No. 4 in Table 1). This value was larger than the stoichiometric ratio (2.5) for Mn_5C_2. However, a similar result was shown by Kor[8)] (Mn/C=2.7) and our gas composition was also coincident with his report. This may be ascribed to the existence of Mn_3C or to the existence of the high valency state Mn in the precipitate. Mn/C was 2.46 for the No. 1 carbide mainly composed of Mn_7C_3. Since Mn_5C_2 phase could be also observed in this specimen, the value of Mn/C may become somewhat higher than the stoichiometric ratio (2.33) for Mn_7C_3.

Furthermore, by substituting the values of $x, y, p, q, \cdots, v$, and w into Eq. 4, the theoretical gas volume evolved from 1 g of the produced carbide can be calculated. For example, from the values of $p=0.4813$, $q=0.3743, \cdots, w=0.0024$ for the No. 1 product in Table 2, the amount of gas was 0.9874 mole $(p+q+\cdots+w)$ per one mole of Mn_xC_y ($x=1.659$, $y=0.675$). Therefore, the theoretical gas volume is calculated to be 243 $cm^3\,g^{-1}$ (at 25 °C) for the No. 1 product. The volume of gas obtained in our experiment (197.8 $cm^3\,g^{-1}$) was lower than this value and the yield may be 81%. In the literature,[10)] the experimentally observed volume for Mn_7C_3 hydrolyzed at 80 °C was 208 $cm^3\,g^{-1}$ and their predicted value was 213 $cm^3\,g^{-1}$. Our yield might be somewhat higher than 81% if we took account of the liquid phase products, which we did not analyze in the experiment. The analysis of the liquid product is in progress.

Recycle of Manganese. After the hydrolysis, the precipitate was filtrated and γ-Mn_2O_3 thus obtained was subjected to the second production of the carbide. The mixture of γ-Mn_2O_3 and graphite in a stoichiometric composition corresponding to Mn_3C was calcined at 1000 °C in vacuum. Unfortunately, only very small amounts of the carbides were formed in this procedure and the gas volume evolved by the hydrolysis was only 9.8 $cm^3\,g^{-1}$ for 50 h firing specimen. The X-ray diffraction patterns of calcined exhibited only MnO and graphite(unreacted starting material). The reduction of MnO with carbon has been studied by many workers.[12—16)] According to Ikeda and Terayama,[16)] the reduction of MnO with graphite into Mn_7C_3 began at about 1050 °C in argon atmosphere and the addition of Fe_2O_3 lowered the reduction temperature. If one can find more effective additives for the reduction of MnO, the yield of the carbides may be increased. We added firstly the alkaline carbonates to the specimen. γ-Mn_2O_3 (prepared from $MnCl_2$ and KOH), graphite and alkaline carbonate were mixed and pelletized with hydrostatic pressure of 2×10^3 kg cm^{-2}. In these experiments, the compositions of starting materials were decided by assuming that following reactions took place to form $(Mn_3C)_x(M_2C_2)_y$.

$$3/2Mn_2O_3 + 11/2C \longrightarrow Mn_3C + 9/2\,CO \qquad (5)$$

$$M_2CO_3 + 4C \longrightarrow M_2C_2 + 3CO\ (M=K, Na, Li) \qquad (6)$$

The specimens were calcined at 1000 °C in vacuum.

Typical results are shown in Table 3. The addition of Na_2CO_3 and K_2CO_3 did not promote the production of the carbide. However, Li_2CO_3 was very effective promoter for carbide formation. For example, when Li/Mn=0.35 (No. 11 in Table 3), the main product after 12 h calcination at 1000 °C was Mn_7C_3 and the volume of gas evolved by hydrolysis at 50 °C was 193 $cm^3\,g^{-1}$, which was close to that obtained for the carbide made from metallic Mn and graphite. Li_2C_2 could not be detected in the products by X-ray diffraction. The composition of product gas was similar to that shown in Table 2. Since neither the appearance of acetylene nor the increase in C_2-hydrocarbon could be detected in this gas, it was considered that the product might not contain Li_2C_2 and that the gas was evolved by hydrolysis of Mn_7C_3.

Effect of Li_2CO_3 on Carbide Formation. In order

TABLE 3. FORMATION OF MANGANESE CARBIDE FROM γ-Mn_2O_3 WITH AND WITHOUT ADDITIVES

No.	Composition	Time/h	Product$^{a)}$	Gas volume$^{b)}$/cm^3 g^{-1}
6	$(Mn_2O_3)_3C_{11}$	50		9.8
7	$(Mn_2O_3)_{1.05}(Na_2CO_3)_{0.30}C_{5.05}$	12	◎ MnO	7.3
8	$(Mn_2O_3)_{1.05}(K_2CO_3)_{0.30}C_{5.05}$	12		8.5
9	$(Mn_2O_3)_{1.35}(Li_2CO_3)_{0.10}C_{5.35}$	12	○ MnO, △ Mn_7C_3	96.0
10	$(Mn_2O_3)_{1.20}(Li_2CO_3)_{0.20}C_{5.20}$	12	○ Mn_7C_3, ▲ MnO	164.5
11	$(Mn_2O_3)_{1.05}(Li_2CO_3)_{0.30}C_{5.05}$	12	◎ Mn_7C_3	193.0

a) Observed phase by X-ray diffraction: The symbols are same as in Table 1. b)Volume of gas at 25 °C and 1 atm(101.3 kPa) evolved by hydrolysis at 50 °C.

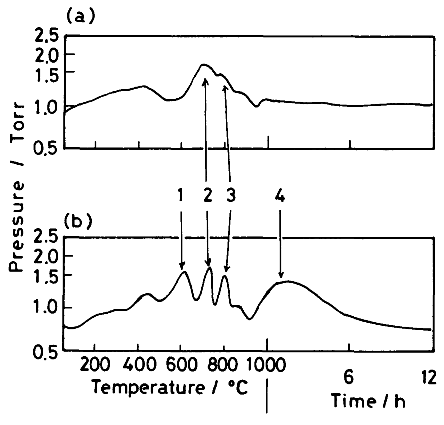

Fig. 4. Change in the total pressure during calcination.*
(a) Mn_2O_3+C ($(Mn_2O_3)_3C_{11}$), (b) $Mn_2O_3+Li_2CO_3+C$ ($(Mn_2O_3)_{1.05}(Li_2CO_3)_{0.30}C_{5.05}$).
* Specimen is heated up to 1000 °C at the heating rate of 200 °C h^{-1} and kept at 1000 °C for 12 h.

to obtain an information about the effect of Li_2CO_3 on the production of Mn_7C_3, the variation of pressure during the calcination was monitored by a vacuum meter (ULVAC, GP-1S). The specimen in the ceramic tube was heated up to 1000 °C at the heating rate of 200 °C h^{-1} and then kept at 1000 °C for 12 h. Since the ceramic tube was evacuated with a vacuum pump at a constant pumping speed, the evolution of gas(CO) could be detected as the increase in the pressure.

Figure 4 shows the change in the total pressure during the calcination with and without addition of Li_2CO_3. In the heating process, appreciable pressure peaks were observed in the temperature range between 600 and 900 °C (peaks 2, 3) in both cases. The peaks 2 and 3 correspond probably to the following reaction steps (Eqs. 7 and 8) since γ-Mn_2O_3 can be reduced to MnO by graphite at these temperatures without Li_2CO_3.[17]

$$Mn_2O_3 + 1/3C \longrightarrow 2/3Mn_3O_4 + 1/3CO \text{ (peak 2)} \quad (7)$$

$$2/3Mn_3O_4 + 2/3C \longrightarrow 2MnO + 2/3CO \text{ (peak 3)} \quad (8)$$

$$Mn_2O_3 + C \longrightarrow 2MnO + CO \quad (9)$$

When Li_2CO_3 was added to the sample ((b) in Fig. 4), additional increases in the pressure were observed at 600 °C (peak 1) and at 1000 °C (peak 4). The peak 1 may be ascribed to the evolution of CO[18] because Li_2CO_3 is easily decomposed to Li_2O at 600 °C in vacuum.

$$Li_2CO_3 + C \longrightarrow Li_2O + 2CO \quad (10)$$

Since the formation of Mn_7C_3 was confirmed after this calcination, the peak 4 should correspond to a reduction step of MnO into Mn_7C_3 which was catalyzed by lithium or Li-compounds ($7MnO+10C \xrightarrow{(Li)} Mn_7C_3+7CO$). Li_2C_2 or metallic lithium should be an effective reducing agent against MnO. Although Li_2C_2 was not detected in the product, appreciable amount of metallic lithium was observed in the ceramic tube after the calcination. Therefore following reaction steps including Li as an intermediator may be possible at peak 4.

$$Li_2O + C \longrightarrow 2Li + CO \quad (11)$$

(1000 °C, under vacuum[2])

$$MnO + 2Li \longrightarrow Mn + Li_2O \quad (12)$$

$$7Mn + 3C \longrightarrow Mn_7C_3 \quad (13)$$

Other posssible reaction steps including Li_2C_2 as an intermediator may be also followed by Eq. 11.

$$2Li + 2C \longrightarrow Li_2C_2 \text{ (950 °C[2])} \quad (14)$$

$$2MnO + Li_2C_2 \longrightarrow 2Mn + 2Li + 2CO \quad (15)$$

$$7Mn + 3C \longrightarrow Mn_7C_3 \quad (16)$$

Anyway, it can be said that lithium is a good catalyzer for reducing MnO to Mn_7C_3, and that "Manganese-Cycle" proposed by us is one of promising methods for the production of hydrogen and hydrocarbons. Carbon monoxide gas during the production of the carbides could be also utilizable. The detailed studies are in progress.

Conclusion

A new carbide method based on "Manganese-Cycle" was studied. In this process, the fuel gas containing hydrogen and hydrocarbons (C_1–C_5) was obtained by the hydrolysis of manganese carbides. And carbon monoxide could also be obtained during the production of the carbides. γ-Mn_2O_3, by-product of the hydrolysis, was recycled as the manganese source effectively by adding Li_2CO_3 in order to promote the carbide formation.

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