Reducing CO_2 Emissions by Using Carburizing Gas Regenerator

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Gas carburized quenching process exhausts much CO_2 because fossil fuels is burned. For this reason, reducing CO_2 is one of the urgent tasks for this process. “carburizing gas regenerator” is an equipment, including polyimide hollow-fiber membrane filter, which allows H_2 to permeate therethrough. As H_2 is generated during carburizing process, by circulating carrier gas using this equipment, H_2 is eliminated by filter, and H_2 eliminated carrier gas is able to reuse to the furnace.

Using carburizing gas regenerator enables to reduce total amount of carrier gas and CO_2 emissions up to 50%, and get less variation of hardness and carbon concentration among carburized quenching specimens.

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1. Introduction

In the conventional gas carburizing process, carrier gas is used at least 6 times of furnace volume per hour [1]. However, only small amount is utilized for carburizing in the introduced carrier gas, and most of it burned and disposed of outside the furnace, resulting in CO_2 emissions. Carburizing reaction produces especially H_2 during process and affects atmosphere compositions. The reason why introducing large amount of carrier gas into furnace is to keep atmosphere compositions stable [2]. If the amount of carrier gas is not enough, it is difficult to control carbon potential (CP) precisely and results in variation of carbon concentration and hardness in the carburized quenching test.

In this study, we conducted gas carburized quenching tests with three conditions: conventional amount of carrier gas, 50% reduction of carrier gas using carburizing gas regenerator and 50% reduction of carrier gas without using carburizing gas regenerator. After that, we compared atmosphere compositions, carbon concentration, hardness and metallographic structure among three conditions.

2. Method of carburizing gas regenerating

2.1 Gas reactions of during carburizing

During gas carburizing, carrier gas (RX gas) containing CO, N_2 and H_2 as main components is used and added enrich gas to control CP. Carrier gas is generated by adding a certain percentage of air to C_3H_8 or C_4H_{10} reacting at temperature around 1323-1373K. The enrich gas is C_3H_8 or C_4H_{10} which is added to carrier gas at small amount.

Carburizing to steel is caused by the reaction of gases containing carbon, mainly CO. Carburizing reaction on the surface of steel is mainly expressed by the following equation.

$$2CO \rightarrow (C)+CO_2 \quad (1)$$
$$CO+H_2 \rightarrow (C)+H_2O \quad (2)$$
$$CH_4 \rightarrow (C)+2H_2 \quad (3)$$

Above (C) represents carbon, carburized into steel. CO_2 and H_2O are generated by carburizing reaction which affect CP. To maintain CP, enrich gas is added.

If C_3H_8 is used as enrich gas, reaction is expressed by the following equation [3].

$$C_3H_8+3CO_2 \rightarrow 6CO+4H_2 \quad (4)$$
$$C_3H_8+3H_2O \rightarrow 3CO+7H_2 \quad (5)$$
$$C_3H_8 \rightarrow 3(C)+4H_2 \quad (6)$$

Reaction of enrich gas and CO_2 generate H_2.

Fig. 1 shows generated H_2 volume during carburizing at 1203K-CP1.15. Total surface area of specimen is 10.8m^2. According to Fig. 1, large amount of H_2 generates at the beginning of carburizing period and decreases gradually.

Fig. 2 shows calculated value of the change of CO concentration in the furnace according to the generated H_2 shown in Fig. 1 when volume of carrier gas is introduced into the furnace 20m^3/h. The carrier gas of 20m^3/h is a general volume of gas carburized quenching process. As the carrier gas is based on C_4H_{10}, initial CO concentration is 23.5%. It can be confirmed that CO concentration decreases due to H_2 generation by carburizing and does not return to 23.5% even after 100 minutes.

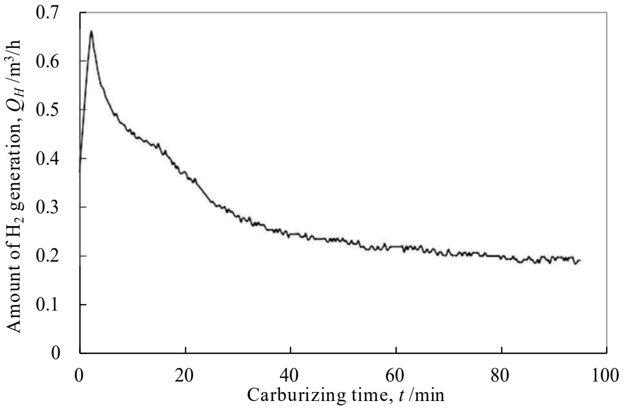


Fig. 1 Amount of H_2 generation during carburizing.

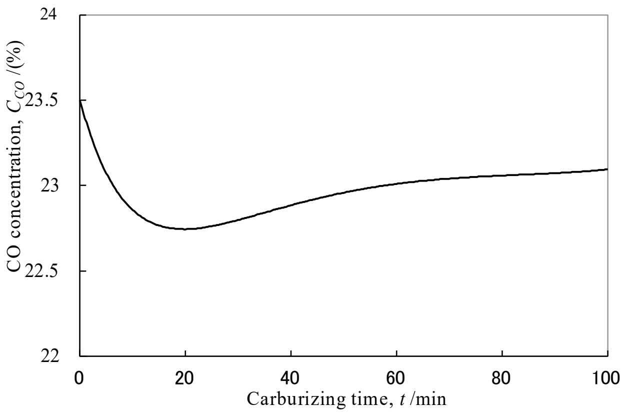


Fig. 2 Calculated change of CO concentration affected by H_2 generation.

In the conventional gas carburizing, a large amount of carrier gas is introduced to mitigate the effect of increased H_2 during carburizing. If carrier gas is reduced to reduce exhausted CO_2, it is difficult to control CP because H_2 increases. Therefore, if the increased H_2 can be removed, carrier gas in the furnace can be reusable (see Fig. 3).

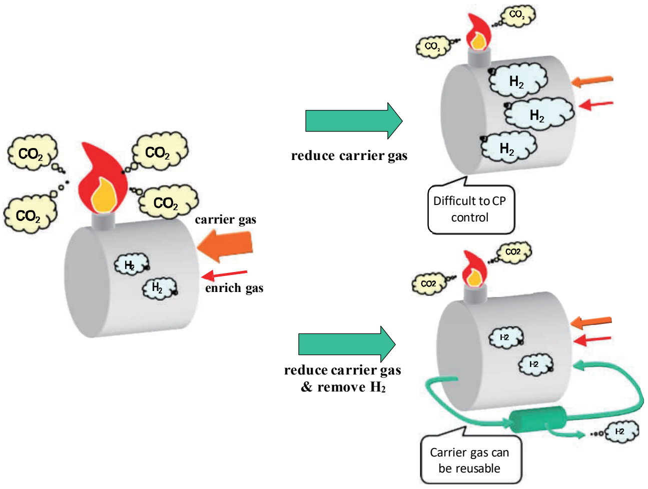


Fig. 3 Concept of reusing carrier gas.

2.2 Constitution of gas regeneration equipment

To regenerate carrier gas, the gas inside furnace is circulated by a circulation pump and H_2 is removed by using "carburizing gas regenerator" at the path of circulation gas, as shown in Fig. 4.

"Carburizing gas regenerator" as shown in Fig. 5 can selectively permeate H_2 through polyimide hollow-fiber membrane filter (see Fig. 6) by using educator pump and exhaust it. Polyimide has excellent thermal stability and mechanical strength, and has high gas separation properties [4), 5)]. Since the atmosphere in the furnace is disturbed when charging the specimen, conventional amount of carrier gas (large flow) is introduced during heating period and holding period to ensure sufficient replacement of atmosphere. Since carburizing period of using carburizing gas regenerator, small amount of carrier gas (small flow) is introduced. To change amount of carrier gas, two switchable flow paths is necessary.

In addition, in order to prevent excessive H_2 exhausting, it is possible to control the amount of H_2 exhausting by controlling CO concentration stable.

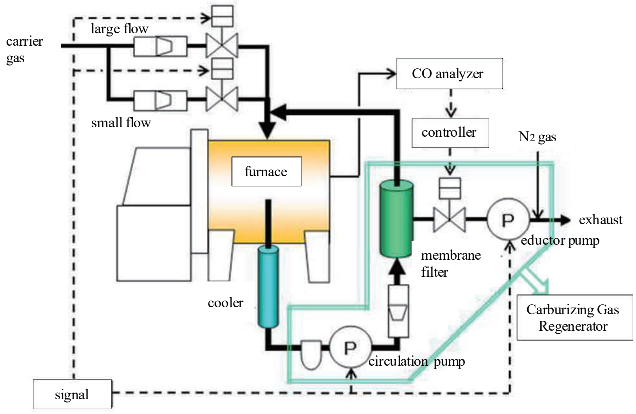


Fig. 4 Constitution of gas regeneration equipment.

(a) Carburizing gas regenerator (b) Control panel

Fig. 5 Appearance of "carburizing gas regenerator".

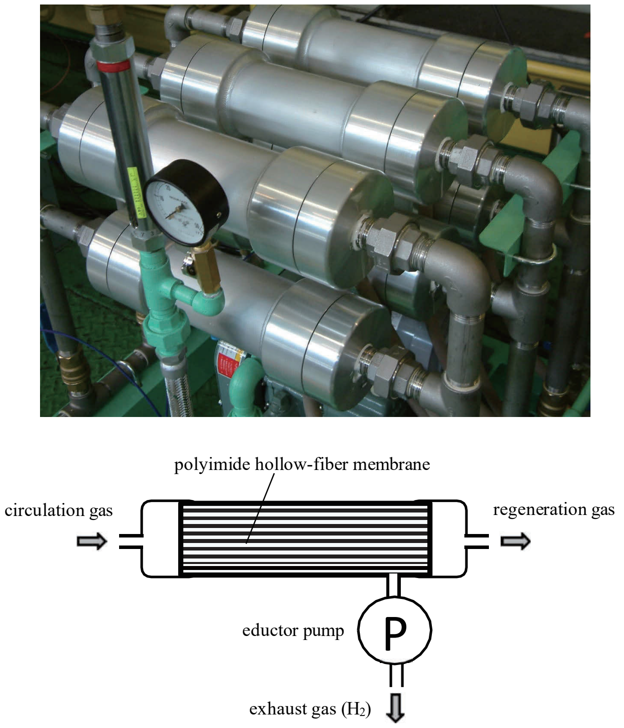


Fig. 6 Polyimide hollow-fiber membrane filter.

3. Experiment

3.1 Specimens

The specimens used for experiment were cylindrical shape (φ18×50mm) and made of chromium steel (JIS SCr420). Chemical compositions of chromium steel (JIS SCr420) is listed in table1.

To investigate carburizing variation, we set corner and center position of loading position. In order to increase the surface area of specimens, we loaded dummy steel plates to make the surface area about 11m^2 as shown Fig. 7.

Table 1 Chemical compositions of chromium steel (JIS SCr420)/ (mass%).

C	Si	Mn	P	S	Cu	Ni	Cr
0.22	0.25	0.68	0.022	0.016	0.12	0.07	1.04

Fig. 7 Loading method of carburized quenching test.

3.2 Test furnace

A batch-type test furnace shown in Fig. 8 was used for carburized quenching test. Effective dimensions were 600mm in width, 600mm in length, 600mm in height, and the maximum load capacity was 200kg. The atmosphere during carburizing was controlled by CP using O_2 sensor. The carrier gas was based on C_4H_{10}, and CP was calculated with a constant CO concentration of 23.5%. About quenching, hot type oil of Daphne Hi Temp Oil A (IDEMITSU) was used as a quenching media.

Fig. 8 Batch-type test furnace.

3.3 Heat treatment condition

Heat cycle of carburized quenching is shown in Fig. 9. Three heat cycle conditions were conducted as below.

(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

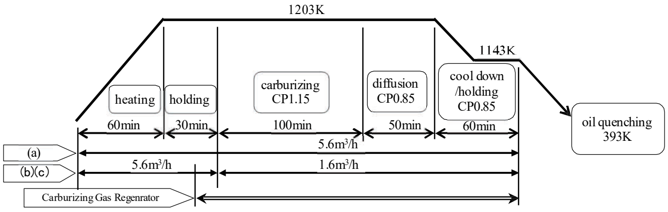


Fig. 9 Heat cycle of carburized quenching.

For (a), the volume of carrier gas was 5.6m^3/h throughout the cycle, for (b) and (c), heating period and holding period were 5.6m^3/h and since carburizing periods were 1.6m^3/h. For carburizing gas regenerator, circulating gas volume was 6m^3/h and the valve of educator pump was controlled to maintain a constant CO concentration of 23.5%.

Total amount of carrier gas was 28m^3 for (a), and 14m^3 for (b) and (c), which were as half as (a).

3.4 Characterization

After carburized quenching test, we measured distribution of hardness with micro vickers hardness tester, metallographic structure with digital microscope and distribution of carbon concentration with EPMA of specimens. Besides, during carburizing, we measured H_2 and CO concentrations of furnace atmosphere with H2 sensor and infrared analyzer.

4. Results

4.1 Verification of H_2 emissions

Before carburized quenching test, we checked the amount of exhausting gas volume in circulating gas and concentration of H_2 contained in the exhausting gas. The results are shown in Fig. 10. As the volume of circulating gas increased, the volume of exhausting gas also increased. Concentration of H_2 in exhausting gas was over 95%.

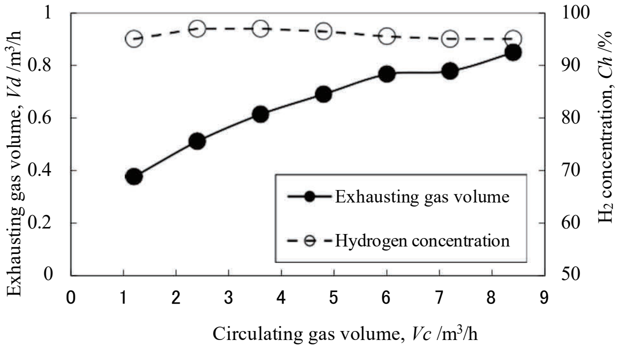


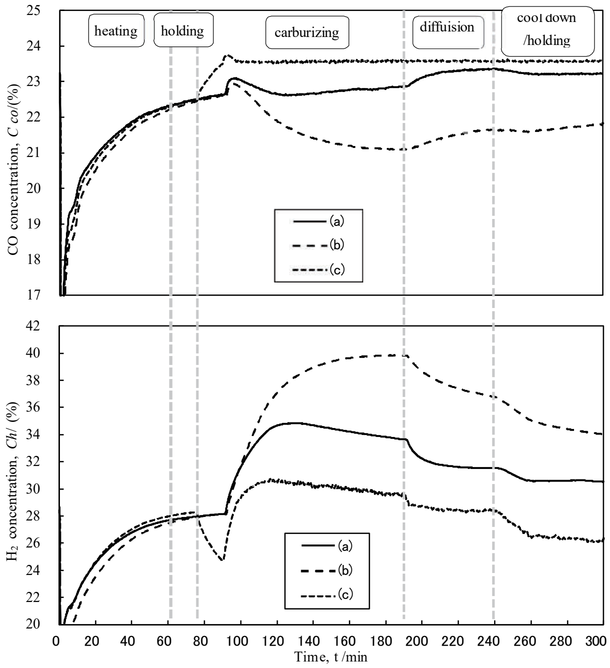
Fig. 10 Exhausting gas volume and H_2 concentration.

4.2 Behavior of the atmosphere

Fig. 11 shows the behavior of CO and H_2 concentrations for (a), (b) and (c) during carburized quenching test.

CO concentration was constant at 23.5% since carburizing period under condition of using carburizing gas regenerator (c). On the other hand, under condition of not using carburizing gas regenerator (b), CO concentration decreased to a minimum of about 21%, and was as low as 22% or less even immediately before quenching. In addition, a slight decrease in CO concentration from 23.5% was observed even with the conventional carrier gas volume (a). Therefore, even in conventional gas volume condition of (a), controlled CP was considered to be slight difference from calculated CP.

Concerning H_2, concentration of H_2 was increased at the same time as carburizing period starts, and was decreased accordingly for (a) and (b). In (c), the increase of H_2 concentration was suppressed and the CO concentration was stable.

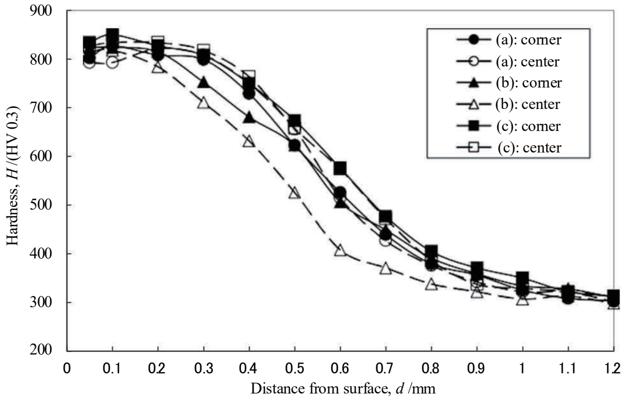


(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

Fig. 11 Behavior of CO and H_2 concentrations.

4.3 Distribution of hardness

The distribution of hardness is shown in Fig. 12, and the effective case depth is shown in Table 2. (b) showed shallower effective case depth than (a) and (c), and variation between center and corner was large. The reason why center position of (b) shallower than corner position is low carbon concentration (see Fig. 14) and low hardenability due to slow flow rate of quenching oil. Compared to (a) and (c), (c) was a slightly deeper effective case depth and less variation. This is probably due to the stable CO concentration in the atmosphere.



(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

Fig. 12 Distribution of hardness of loading position.

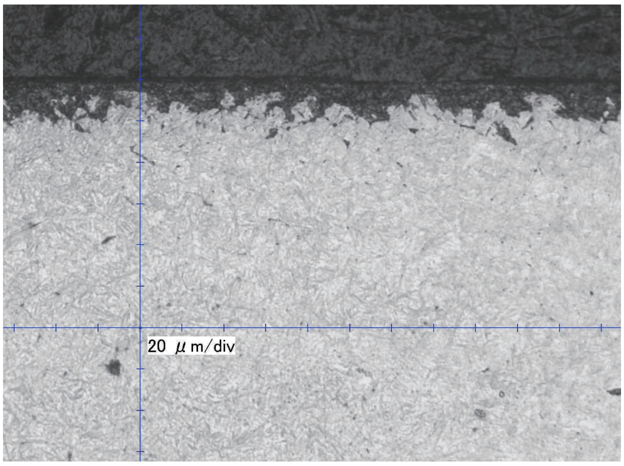
Table 2 Effective case depth of loading position.

	Effective case depth, *de*/mm	
	Corner	Center
(a)	0.57	0.57
(b)	0.56	0.48
(c)	0.63	0.62

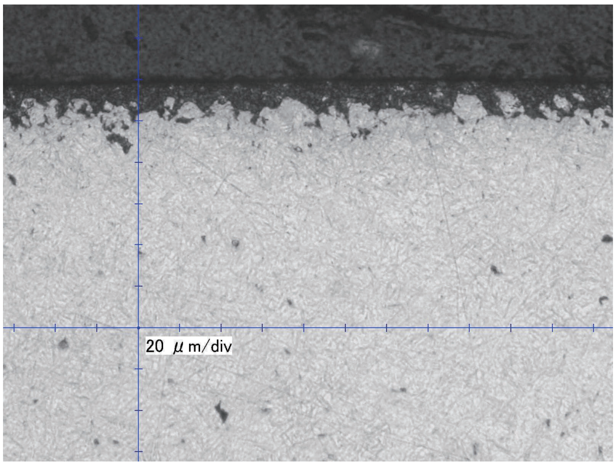
(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

4.4 Metallographic structure

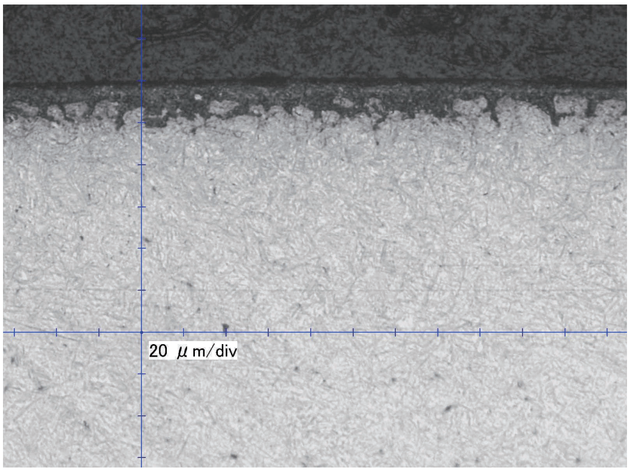
Fig. 13 shows metallographic structure of (a), (b) and (c). All conditions show martensite structures and no differences.



(a) Condition (a)



(b) Condition (b)



(c) Condition (c)

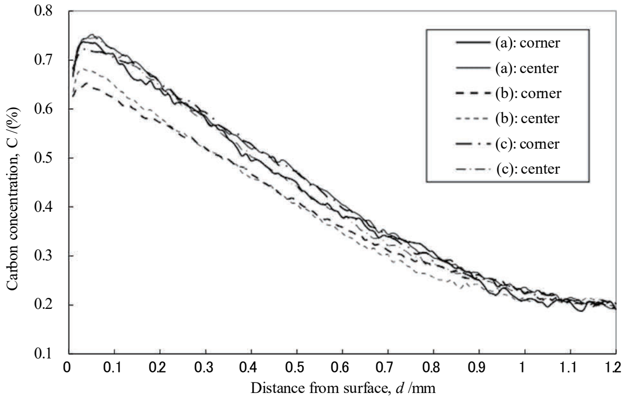
(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

Fig. 13 Metallographic structures.

4.5 Distribution of carbon concentration

Fig. 14 shows the distribution of carbon concentration, and Table 3 shows 0.35wt% carbon concentration depth. As with the distribution of hardness, (b) had a shallower distribution of carbon concentration than (a) and (c), and showed variation near surface.

From results of Fig. 14 and Table 3, the reason why effective case depth of (b) in Fig. 12 and Table 2 was shallow was caused by shallower carbon concentration. Shallow carbon concentration was due to inaccurate CP control because amount of carrier gas was not enough.



(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

Fig. 14 Distribution of carbon concentration.

Table 3 0.35wt%C depth of loading position.

	0.35wt%C depth, *dc*/mm	
	Corner	Center
(a)	0.57	0.61
(b)	0.52	0.51
(c)	0.60	0.57

(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

4.6 The amount of CO_2 emissions

The amount of CO_2 emissions generated by exhausted carrier gas at this test, using a formula of Japanese Ministry of the Environment was open to the public [6)], were 14kg in (a), 7kg in (b) and (c), which were reduced 50% to (a).

5. Discussion

Fig. 15 shows minimum volume of carrier gas when using carburizing gas regenerator. The minimum volume of carrier gas represents the limit at which the furnace pressure and atmosphere can be maintained when using carburizing gas regenerator. According to Fig. 15, the smaller total surface area of specimens and lower CP, the smaller minimum volume of carrier gas, this results in more carrier gas can be reduced.

Table 4 shows the calculated results of CO_2 emissions in actual production process. In this simulation, carrier gas volume of conventional process is assumed $20m^3/h$. In case of using carburizing gas regenerator, carrier gas volume is used of Fig. 9 at total surface of specimen 10, 15 and $20m^2$. Annual operating time is assumed as 24 hours*300 days. As a result, by using carburizing gas regenerator, annual CO_2 emission can be reduced by more than 50%.

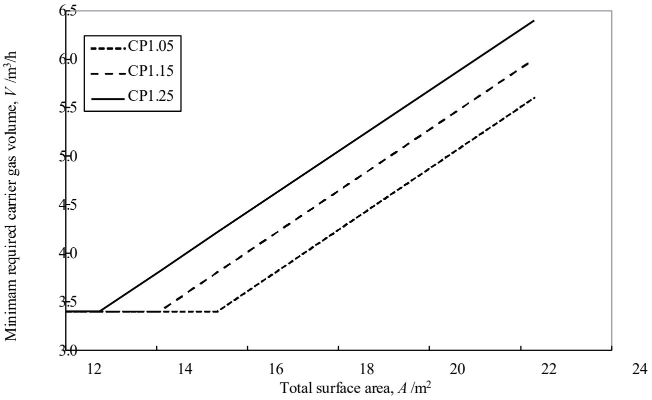


Fig. 15 Minimum volume of carrier gas.

Table 4 Annual CO_2 emissions.

	Total surface area, A /m²	Amount of total carrier gas, Q /(m³/ch)	Annual CO_2 emissions, E /t	CO_2 emission ratio
(a)	-	100	73.6	1.0
(b) (c)	10	41.90	30.9	0.42
	15	42.25	31.1	0.42
	20	48.55	35.8	0.49

(a) Base condition:
Volume of carrier gas is conventional.
(b) Reduce carrier gas:
Not using carburizing gas regenerator.
(c) Reduce carrier gas:
Using carburizing gas regenerator.

6. Assignment

For gas carburizing process, it is possible to reuse carrier gas by using carburizing gas regenerator at batch-type furnace. But following assignments still remain.

(1) As polyimide hollow-fiber membrane filter does not have NH_3 resistance, carburizing gas regenerator cannot use at atmosphere including NH_3, such as carbonitriding process.

(2) For continuous gas carburizing furnaces, circulation carrier gas of carburizing gas regenerator may affect original gas flow in the furnace and result in disturbing atmosphere in the furnace. Therefore, some attention is necessary when using carburizing gas regenerator for continuous gas carburizing furnaces.

7. Conclusions

The carburized quenching test using carburizing gas regenerator was conducted and got following results.

(1) Compared to conventional carburized quenching, total amount of carrier gas could be reduced by 50%, and distribution of both hardness and carbon concentration were deeper and less variation than conventional results.

(2) In case of reducing carrier gas not using carburizing gas regenerator, distribution of both hardness and carbon concentration were shallow, and showed variation.

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