

CO₂ Separation in Syngas Obtained from Gasification of Waste by Adsorption Method

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ABSTRACT: The interest related to the syngas produced from gasification of solid feedstock is rapidly growing in recent years. The main components of syngas produced from gasification are hydrogen(H₂), carbon monoxide(CO), carbon dioxide(CO₂), moisture(H₂O). To utilize this raw syngas efficiently as fuel or chemical feedstock, CO₂, H₂O and minor contaminants should be removed. Especially, as a significant greenhouse gas, CO₂ separation and capture is a very important issue in terms of greenhouse gas control. So, there are many research and development for the separation and capture of CO₂ to minimize the emissions of CO₂ with lower costs. One of the most widely used adsorbents for CO₂ separation is zeolites with a high surface area and its three-dimensional pore structure is expected to result in a high performance adsorbent for CO₂ removal. In this study, to separate CO₂ in syngas from gasification of waste, the experiments were carried out to investigate the characteristics of CO₂ adsorption and desorption using NaX zeolites.

Keywords: Waste, gasification, carbon dioxide, adsorption, NaX zeolite

NOMENCLATUR

PSA : Pressure Swing Adsorption

VSA : Vacuum Swing Adsorption

TSA : Temperature Swing Adsorption

TPD :Temperature Programmed Desorption

TCD : Thermal Conductivity Detector

1. INTRODUCTION

The main components in syngas from gasification of waste are hydrogen(H₂), carbon monoxide(CO), carbon dioxide(CO₂), moisture(H₂O). The heating values of these fuel gases are typically about 1,500 – 2,000 kcal/Nm³. To utilize this raw syngas high efficiently as fuel or materials for chemical products, it must be removed CO₂ and minor contaminants. Especially, as a significant greenhouse gas, CO₂ separation and capture is a very important issue and a major

problem. Moreover, the heating values of the syngas after CO₂ separation are over 2,500 kcal/Nm³ and the stability of combustion as fuel is improved. To utilize the syngas obtained from gasification of waste as fuels for gas engine more efficiently, it was considered the application of the CO₂ separation process in waste gasification system as shown in Fig. 1.

Four different CO₂ removal technologies are widely practiced in industry[1]. These are absorption, both chemical and physical adsorption, membranes, and cryogenic processes. In this study, to separate CO₂ in syngas from gasification of waste, the adsorption method was considered. In the last two decades, active research efforts have been done on the separation of carbon dioxide by adsorption processes and this technique has been developed for commercial applications.

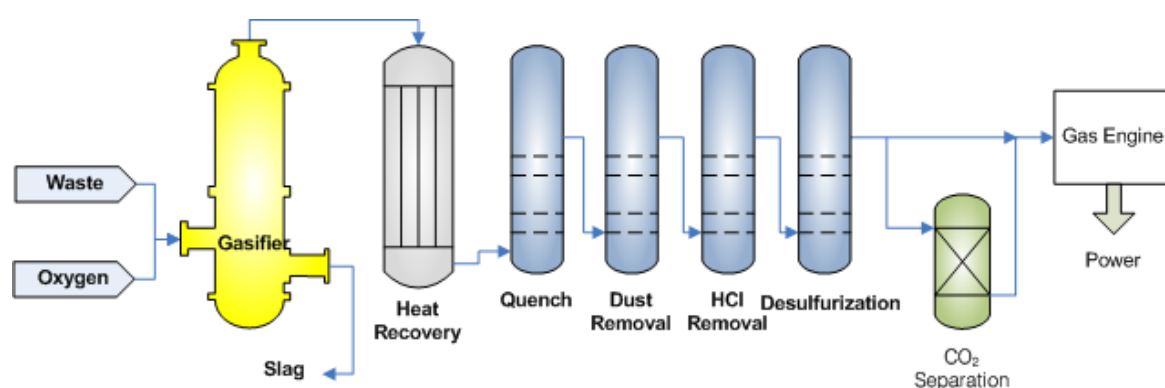


Fig. 1. Process flow diagram of waste gasification system

Effective CO₂ adsorbents are required for the processes and the choice of adsorbent becomes the most important design consideration for separation methods based on adsorption processes. One of the most widely used adsorbents for CO₂ separation are zeolites with a high surface area and a three-dimensional pore structure. These have been expected to be a high performance adsorbent for CO₂ Syngas produced from gasification of waste. Recent investigations based on zeolite adsorbent screening revealed that the most suitable zeolites are characterized by a narrow pore size, low Si/Al ratio and should contain specific type of extra-framework cations interacting with the CO₂ molecules. In this study the experiments of CO₂ adsorption and desorption were carried out to determine the characteristics of CO₂ adsorption and desorption on NaX type zeolite adsorbent. The adsorption and desorption behavior of CO₂ was investigated by TPD method and lab-scale experimental apparatus.

2. EXPERIMENTAL METHODS

2.1 Materials

The sample material used during the experiments was NaX type zeolite adsorbent with 2 mm diameter. The bulk density, BET surface areas, average pore diameter and maximum pore volumes were measured. The measured physical properties of the sample material are listed in Table 1.

Table 1. Physical properties of NaX type zeolites

Property		NaX type zeolite adsorbent
Bulk density(kg/m ³)		609
BET surface area(m ² /g)		418
Average pore diameter(Å)		0.76
Maximum pore volume(cm ³ /g)		0.16
XRF analysis (wt.%)	Na ₂ O	19.15
	MgO	2.05
	Al ₂ O ₃	29.55
	SiO ₂	46.95
	K ₂ O	0.24
	CaO	0.77
	Fe ₂ O ₃	0.31
	CuO	0.17
Si/Al		1.59

2.2 Apparatus and Procedure

First, we tested whether that the sample adsorbents removed only CO₂ in syngas. Syngas composition was CO₂ 6.8%, H₂ 5.9%, N₂ 27.9%, CO 59.4% and while these syngas passed through adsorbents, gas composition after passing through the adsorbent samples was analyzed by GC.

Also, to verify the CO₂ selective adsorption of the sample adsorbent, the gas composition produced by heating the adsorbent sample after adsorption test was analyzed using GC. To investigate the adsorption and desorption characteristics of CO₂ on NaX zeolite samples, the adsorption test was executed with various gas type and composition by TPD method and lab-scale experiments. TPD is the method to measure the status of physical adsorption and chemisorption. It can be obtained by measuring desorption or decomposition of adsorbed molecules from the surface while continually heated. By TPD, it can be determined the number of desorption peaks from the spectrum of desorbed molecules, desorption temperature, and volume of desorption. Adsorption of probe molecules to the sample is generally done by pulse injection method, volumetric method under the vacuum, or flow method. Although the condition of measurement varies in each case, desorption measurement can be basically done by heating under the carrier gas flow. Desorbed gas can be detected by Thermal Conductivity Detector[2]. The principle of TPD method and the apparatus of it are shown in Fig. 2 and Fig. 3.

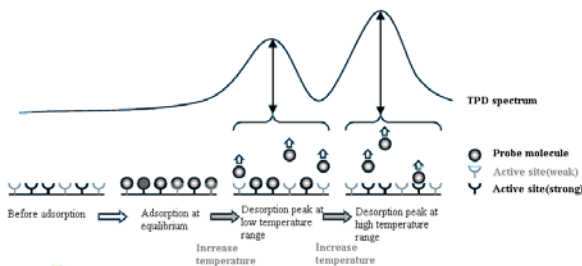


Fig. 2. The principle of TPD method

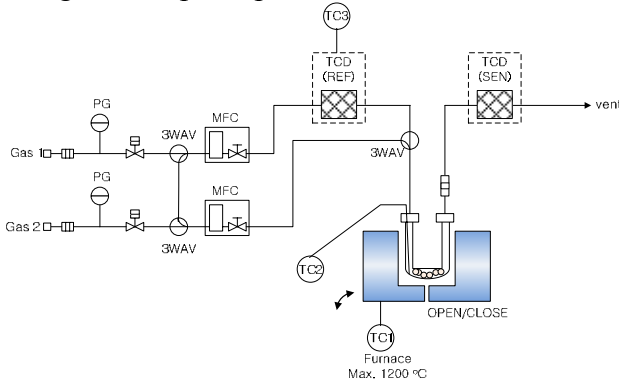


Fig. 3. The apparatus of TPD method

In case of the test by lab-scale experiment apparatus, CO₂ adsorption volumes was evaluated with normal pressure and 6 atm. The gas flow rate was about 0.5 Nm³/h and the gas composition passing through the adsorbent materials was analyzed by on-line gas analyzer. The experiment apparatus of lab-scale is shown in Fig. 4. TPD and lab-scale test conditions to investigate the adsorption volumes of the samples were listed in Table 2.

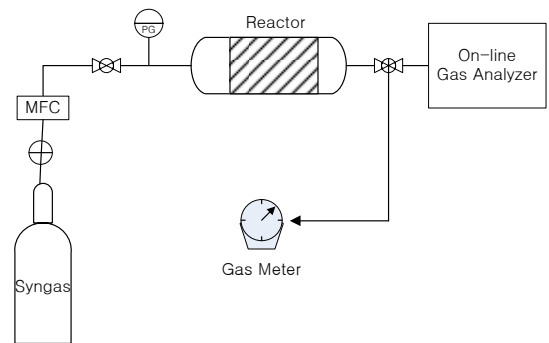


Fig. 4 The apparatus of lab-scale test

Table 2. Adsorption test conditions

Gas type	Pressure	Gas Composition	Method
CO ₂ gas	Normal	CO ₂ 1% He Balance	TPD
CO ₂ gas	Normal	CO ₂ 30% He Balance	TPD
Syngas	Normal	CO ₂ 1% H ₂ 1% CO 1% CO ₂ 30%	TPD
Syngas	Normal	H ₂ 30% CO 30% CO ₂ 30%	TPD
Syngas	Normal	CO ₂ 30% H ₂ 30% CO 30%	Lab-scale
Syngas	6 atm	CO ₂ 30% H ₂ 30% CO 30%	Lab-scale

The desorption test was executed to examine the effect by temperature at 100 °C, 150 °C, 200 °C and 250 °C by TPD method. Holding times were 10, 20, 30 and 60 minutes at each temperature condition. The desorption test conditions were shown in Table 3.

Table 3. Desorption test conditions

Set point (°C)	Set point Holding time (min)	Set point (°C)	Set point Holding time (min)
100	60	200	60
	30		30
	20		20
	10		10
150	60	250	60
	30		30
	20		20
	10		10

3. Results and Discussion

As the test result for the verification of selective adsorption of CO₂ in syngas, we confirmed the selective adsorption of CO₂ on sample adsorbents as shown in Fig. 5 and Fig. 6. The analysis of gas composition showed that the gas adsorbed on NaX type zeolite during the adsorption test using syngas was almost CO₂ gas.

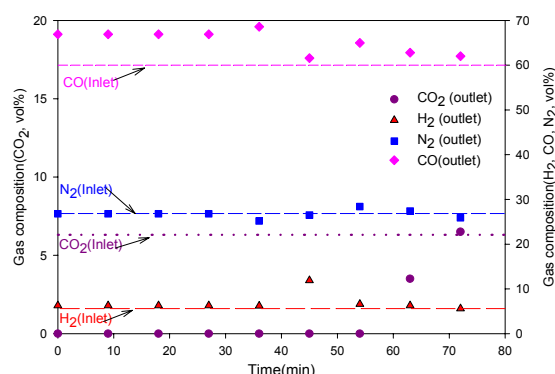


Fig. 5. Gas composition after passing through adsorbents

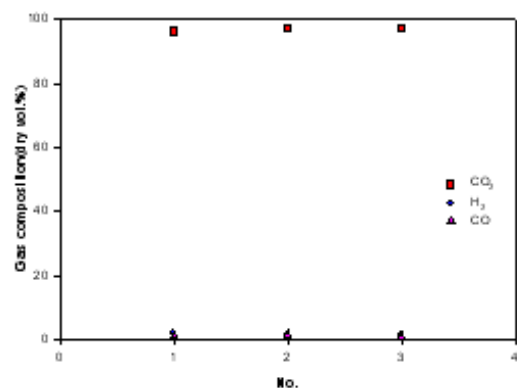


Fig. 6. gas composition produced by heating adsorbents after adsorption test

As the TPD test results, adsorption volumes of CO₂ on NaX type zeolite adsorbent were 115-122 ml/g in case that adsorption gas was only CO₂. In case of the mixture of CO/H₂/CO₂, adsorption volumes of CO₂ were 82-87.6 ml/g. Also, the adsorption test was conducted by lab-scale apparatus using the mixture of CO/H₂/CO₂, adsorption volumes were 57.9 ml/g in case of normal pressure and 71.1 ml/g in case of 6 atm. Adsorption test results were listed in Table 4.

Table 4. Adsorption test results

Pressure	Gas Composition	Method	Adsorption volumes(ml/g)
Normal	CO ₂ 1% He Balance	TPD	115
Normal	CO ₂ 30% He Balance	TPD	122
Normal	CO ₂ 1% H ₂ 1% CO 1%	TPD	82
Normal	CO ₂ 30% H ₂ 30% CO 30%	TPD	87.6
Normal	CO ₂ 30% H ₂ 30% CO 30%	Lab-scale Test	57.9
6 atm	CO ₂ 30% H ₂ 30% CO 30%	Lab-scale test	71.1

As the desorption test results were listed in Table 5 and Fig. 7. Desorption volumes were different from temperature and holding time at the set temperature. The more temperature and holding time at the set temperature increased, the more desorption volumes increased. In case of 100 °C, if the holding time was 60 minutes, desorption volumes were below 50% of the maximum adsorption volumes. But, in case of 250 °C, if the holding time were just over 20 minutes, desorption volumes were almost 100% of the maximum adsorption volumes. From these results, to desorb the CO₂ gas completely by only increasing temperature of adsorbents, temperature and holding time should be over 250 °C and 20 minutes.

Table 5. CO₂ desorption test results

Set point (°C)	Setpoint Holding time (min)	CO ₂ Desorption volume (ml/g)	CO ₂ Desorption volume/Maximum CO ₂ adsorption volume (%)
100	60	47.49	41.3
	30	33.82	29.4
	20	30.46	26.5
	10	19.78	17.2
150	60	87.81	76.4
	30	78.18	68
	20	74.37	64.7
	10	62.37	54.2
200	60	99.01	86.1
	30	101.02	87.8
	20	90.94	79.1
	10	86.91	75.6
250	60	120.52	104.8
	30	115.75	100.7
	20	114.24	99.3
	10	102.14	88.

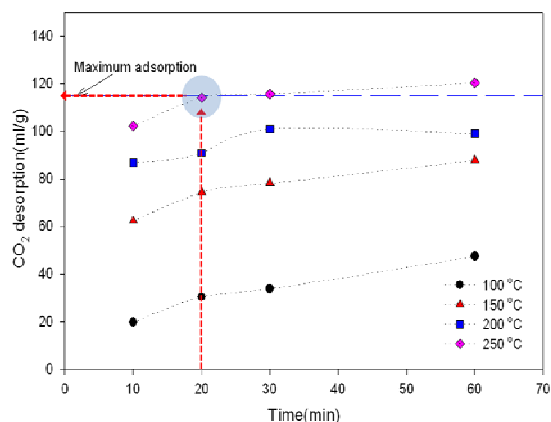


Fig. 7 Desorption test results

5. CONCLUSION

First, we check up the selectivity of CO₂ in syngas of adsorbents to consider the application by the adsorption method for the CO₂ separation in waste gasification system. As the adsorption test results using syngas produced from gasification, the adsorbents adsorbed only CO₂ gas of mixture of CO, CO₂, N₂, H₂.

The characteristics of adsorption and desorption on NaX type zeolite adsorbents with 2 mm diameter were measured by TPD method and lab-scale test. As the TPD test results, adsorption volumes of CO₂ on NaX type zeolite adsorbent were 115-122 ml/g in case that adsorption gas was only CO₂. In case of syngas, adsorption volumes of CO₂ were 82-87.6 ml/g. Also, the adsorption test was conducted by lab-scale apparatus using syngas. Adsorption volumes were 57.9 ml/g in case of normal pressure and 71.1 ml/g in case of 6 atm.

Desorption tests by TPD were carried out at various temperatures and holding time at the set temperature. As desorption test results, the more temperature and holding time at the set temperature increased, the more desorption volumes increased.

Especially, to desorb the CO₂ gas completely from the adsorbents by only increasing temperature, temperature and holding time at the set temperature should be over 250 °C and 20 minutes.

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