Simulated Flue Gas Feed on Coals for Attraction of Subcritical CO_2

Emmanuel Emem-Obong Agbenyeku, Edison Muzenda and Innocent Mandla Msibi

Abstract—In recent years, attention has been drawn towards decreasing the effusion of anthropogenic carbon dioxide (CO_2). CO_2 sequestration is one approach used to reduce its concentration in the atmosphere. This is often the case in deep and inaccessible coal seams where underground storage techniques i.e., flue gas and CO_2 injection under feeds of subcritical and supercritical settings are required. In a bid to reducing carbon footprints, subcritical CO_2 affinity of two sample coal types (sample A-anthracite and sample B-bituminous) in South Africa was evaluated from adsorbates of flue gas and pure CO_2. Volumetric approach using 35˚C and 5MPa was used to measure the attraction/adsorption isotherms of the flue gas and pure CO_2 respectively. Measurements were carried out on 5g samples all passing the 2.36mm American standard sieve size while the flue gas was simulated from industrial coal fired plant having CO_2 = 96.2%, O_2 = 1.5% and N_2 = 2.3% in a high pressure CO_2 volumetric adsorption apparatus. From the generated data, regression models for attraction isotherm were used to resolve the fitness of coal as CO_2 adsorbent. Thus from the study, it was realized that the coal attraction of CO_2 was not notably altered on introduction of other gases. However, sample-A showed a higher adsorption capacity over sample-B, as has been recorded from similar studies. The data herein could therefore, add to the basis for assessing flue gas and pure CO_2 sequestration on South African coal.

Keywords—*Flue gas, Coal, Subcritical, Industrialization, Pure CO_2*

I. INTRODUCTION

THE issues on global warming and environmental changes has been a major concern for most countries in recent years. Changes in ocean currents, volcanic emissions and most especially greenhouse gas effects amongst others are insistently impacting the environment. It has become established that rising levels of atmospheric greenhouse gas from industrial and other anthropogenic activities is drastically altering the global climate system with consequential effects on the health of the environment and inhabitants. As notably recorded by [1] anthropogenic CO_2 effusion is in the frontline of this dreadful impact causing the warming of the earth's atmosphere. On one hand, global industrialization and technological growth in recent times have seen CO_2 effusion from flue gases and other sources rapidly increase such that; between 1800 and 2010, atmospheric CO_2 levels rose from $\geq$ 280 to $\geq$ 379ppm as reported by [2]. Also, the concentration of atmospheric CO_2 is estimated to cause 1.5-4.5ºC surface warming if allowed to double, with the fear that fossil fuel burning could trigger two to three times this effect if not radically controlled [3]. On the other hand, human activities emit CO_2 quit lesser than large natural cycles exchanging CO_2 between the atmosphere, oceans, and terrestrial biosphere. However, as stated by [4] it is clear that the ability for natural systems to absorb the total effusions experienced is insufficient. As such, an optional approach to tackle these insistent environmental challenges through sequestration and isolation of CO_2 is imperative. CO_2 sequestration in deep and inaccessible coal seams appears a cost reduction factor for most mines but most especially, a potential approach to curbing the hazardous emission of CO_2 to the surface. A total estimated CO_2 storage capacity in the South African coal fields is 1271.9Mt as reported by [5] from a geological survey. Although this is based on techno-economics, it must be ensured that stringent measures are taken into mining these coal beds in the future. As reported by [6] South Africa at a time had no obligatory observance of greenhouse gas reduction as it conformed to the Kyoto Protocol as a non-Annex I country. Nevertheless, that protocol was to end in 2013 with considerable pressure from developed countries on non-Annex I countries to develop ways of decreasing effusion of greenhouse gas as per the Kyoto Protocol [7]. In a bid for carbon capture and isolation, it was pertinent to ascertain in-country potentials which according to [8] Department of Minerals and Energy through CSIR showed that the country was up to the task. In this light, few projects have considered the direct injection of flue gases from power plants and other anthropogenic activities. This gave the study the impetus to investigate the adsorption behaviour of CO_2 on two South African coal types with introduced impurities fed as simulated flue gas.

II. CONCEPTUAL AND EXPERIMENTAL APPROACH

A. Testing Method and Setup

A Volumetric approach using 35˚C and 5MPa was used to measure the attraction/adsorption isotherms of the flue gas and pure CO_2 on the two (anthracite and Bituminous) tested coal

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samples. A high pressure CO_2 volumetric adsorption setup used in the study consisted of:

i. reservoir chamber,
ii. sorption chamber,
iii. sample dryer, and
iv. digitized temperature and pressure control system.

The gas composition was measured before and after the multicomponent adsorption tests using SRI instruments Gas Chromatograph (GC – Model 8610C) attached to the high pressure volumetric adsorption setup while a data logging system was used to collect the temperature and pressure values at intervals 0.3sec.

B. Sample Analysis and Preparation

Due to accessibility constraints, only two different coal types were sampled from different coal basins around South Africa and used for the study. For the purpose of this study, the samples were denoted as A and B for the anthracite coal and bituminous coal respectively. Table I shows the petrographic and proximate properties of the tested coals as the samples were characterized by mineral composition, chemical composition (proximate analysis) and coal rank (vitrinite reflectance).

TABLE I
PETROGRAPHIC AND PROXIMATE COAL PROPERTIES

ID	Petrographic analysis (%)				Proximate analysis (%)			
	Maceral matter	Vitri nite	Inerti nite	Lipti nite	Vol. of matter	Ash	Fixed C	H_2O
A	4.5	30	62.1	-	5.5	8.4	82.7	1.1
B	2.2	8.9	72.1	8.2	57.7	17.4	28.3	4.7

C. Test Procedure

Outside all confirmatory tests carried out in the study, two major tests for the respective coal types were done involving systematic approaches that included:

i. sample degassing;
ii. loading the reactor chamber and putting it under vacuum prior gas injection;
iii. finding void volume (*Vvoid*) of the coal loaded reactor, after which the tests were ran.

The coal samples were dried and ground with all samples passing the 2.36mm size sieve in accordance to [9] used for the test. The degassing process was done with the coal samples subjected to vacuum pressure and temperature of -0.07MPa and 130ºC for 2hrs as done by [7]. To equilibrate the system and determine the gas *Vvoid*, helium was first injected knowing that helium will not be adsorbed. As such, in conformance to [10] the temperature, pressure and quantity of injected helium in the chamber were measured after which the injected helium was ejected and replaced by the adsorbate of flue gas or CO_2. It was realized that at pressure of 5MPa the adsorption of CO_2 had reached equilibrium at ≥ 120mins. Close outcomes for similar tests were however, reported by [7] for initial tests of ≥ 19hrs to arrive equilibrium at ≥ 90min of CO_2 adsorption. The attracted gas was then measured from recorded pressure and temperature data.

D. Approach to Fundamental CO_2 Component Adsorption

Gibbs model offers the most fundamental approach to estimating adsorption of gas. The quantity of gas adsorbed (*Nsorbed*) denotes the difference between the total quantity of gas (*Ntotal*) available in the system and the quantity occupied by the *Vvoid*, i.e., the volume not occupied by the solid sample. As noted by [11] the model assumes a constant ratio of condensed phase volume and void volume with no further assumptions for excess adsorption over the span of the testing. Hence, the Gibbs model represented in (1) was used to calculate the excess amount of adsorbed CO_2 from the mass balance between the reference and sample chambers at every gas expansion level.

$$N_{sorbed}^{excess} = \frac{N_{total} - \rho_{eqb} V_{void}}{M_s} \tag{1}$$

Where; N_{sorbed}^{excess} = excess amount adsorbed (mmol/g), N_{total} = total injected amount in the system (mmol), ρ_{eqb} = density of gas as in the case of CO_2 (mmol/cm^3), *Vvoid* = void volume of loaded reactor (cm^3) and M_s = mass of sample (g). In this study the amount of gas adsorbed was expressed in the absolute form with CO_2 value fixed for the model at 22.6mmol/cm^3 as applied by other researchers. Also, the CO_2 densities for ρ_{eqb} and ρ_{gas} at a given T and P in the gas phase were obtained in accordance to [7] while the adsorbed phase density was left constant over the testing period. The conditions of testing herein have been previously applied by other authors and found to be adequate [7], [12] and [13]. Although, it is observed that the calculated absolute adsorption isotherms were affected by the adsorbed-phase density estimates.

E. Multicomponent Gas Adsorption Method

As earlier stated, volumetric approach using 35˚C and 5MPa temperature and pressure respectively, was used to measure the attraction/adsorption isotherms of the flue gas mixture on coal. Measurements were taken for one feed of the simulated gas mixture composition as per [7] with the mixture analyzed after collection from the chamber using a 5ml syringe. To validate the homogeneity of the gas mixture composition in the chamber, Gas Chromatograph Analysis Method (GCAM) was used. On reaching equilibrium for every expansion level; which for this study was recorded at ≥ 120mins, the idle/roaming gas (which was not adsorbed) in the sample chamber was collected through a pipe linking the gas chromatography analyzer and sample chamber. The idle gas was tested to quantify the individual gas components present.

F. Langmuir Isotherm Model for Regression Analysis

For the purpose of predicting gas adsorption/attraction on coal, the Langmuir isotherm regression model is most commonly applied as represented in (2). As recorded by [14] the assumptions made for this model are that:

i. adsorption takes place on an even surface;

ii. at equilibrium, molecule bombardment process continues on the surface;

iii. there is maintained net zero rate of accumulation at the surface for corresponding evaporation of molecules from the surface; and

iv. there is homogeneity at the surface i.e., over all surfaces, adsorption energy is constant.

$$V = \frac{V_L KP}{1 + KP} \qquad (2)$$

Where; V = adsorption volume, V_L = Langmuir volume, K = Langmuir constant and P = pressure. The Langmuir adsorption isotherm is appreciated for its simplicity and is often used in scientific research than any other. However, the aforesaid is not for multicomponent systems but for single gas system. As such, the Langmuir model is further developed to satisfy other CO_2 replacement needs as noted by [8]. When extended to mixed-gas adsorption assuming no interaction among the adsorbed molecules, the Langmuir model becomes:

$$V_i = \frac{V_{L,i} K_i x_i}{1 + \sum_{j=1}^{N} K_j P x_i} \qquad (3)$$

Where; V_i = quantity of component $_i$ adsorbed, x_i = mole fraction of i in the gas, P = pressure, $V_{L,i}$ and K_i = Langmuir constants for i.

III. DISCUSSION OF FINDINGS

A. CO_2 Component Adsorption

In this study, sample-A (Anthracite coal) was found to have steady higher CO_2 adsorption/attraction capacity as compared to sample-B (Bituminous coal) across all measured pressures. The sample-B had considerably the lowest sorption capacity while sample-A was highest even when compared to other coal types in similar studies. Thus, findings herein are in close agreement with results from research by [7], [12] and [13]. Therefore, Fig. 1 shows the relationship between pressure (MPa) and the CO_2 adsorption capacity (mmol/g) on coal for samples-A and B.

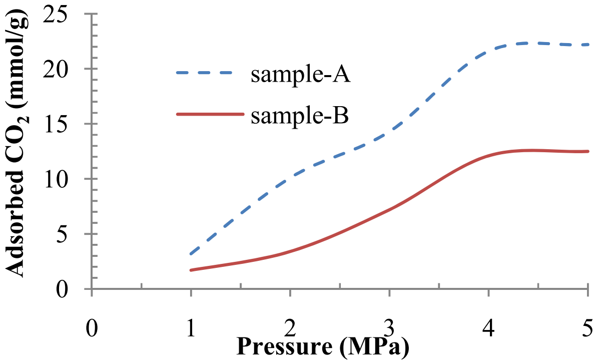

Fig. 1. Pure CO_2 adsorption isotherms (mmol/g)

B. Multicomponent Gas Adsorption

For this study, the predicted adsorption capacities of the multicomponent mixture using equations from the regression model varied over a wide margin from the generated data as such was disregarded. Hence, the discussions herein are based on the analysis of the graphically represented data with respect to the adsorption capacities of the investigated CO_2, O_2 and N_2 simulated gas mixture. Ternary multicomponent gas mixture of; CO_2 = 96.2%, O_2 = 1.5% and N_2 = 2.3% fed on two sampled coal types from South Africa were subjected to 35ºC and 5MPa temperature and pressure respectively. The adsorption of multicomponent gas mixtures on coals is considered a competitive process having very active molecular bombardment between components and surfaces. From Fig. 2, it can be seen that sample-A (the anthracite coal) had strong affinity for CO_2 and recorded a higher adsorption in contrast to, sample-B (bituminous coal) shown in Fig. 3, where a lower preference for CO_2 adsorption across the pressure levels was observed.

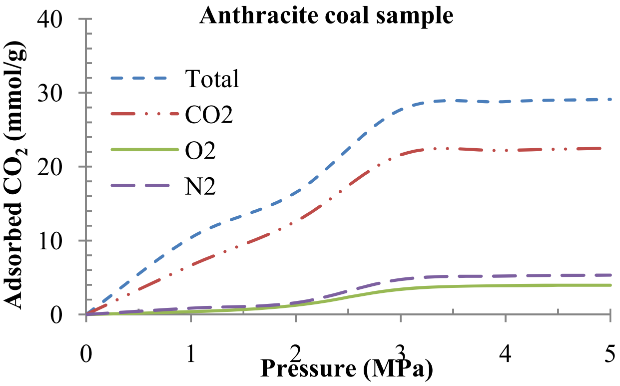

Fig. 2. Multicomponent gas adsorption isotherms (mmol/g) for sample-A

Nonetheless, it was generally observed, that both samples-A and B respectively, showed considerably weak affinity for the other gas components i.e., O_2 and N_2 gases. Therefore, a low adsorption was recorded across the pressure levels. On the addition of O_2 and N_2 as impurities, CO_2 adsorption capacity by the samples was observed to decrease significantly as against the case for pure CO_2 sorption capacity for both samples.

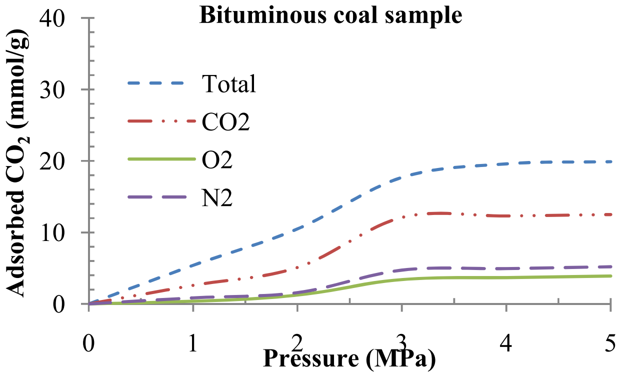

Fig. 3. Multicomponent gas adsorption isotherms (mmol/g) for sample-B

Nevertheless, it was generally noted that the CO_2 adsorption capacities decreased by approximately 15% which was found to be in line with similar studies by [7] where 12% decrease was reported. The O_2 adsorption however, was found to be slightly lesser than the N_2 for both samples across the pressure levels.

IV. CONCLUSIONS

Carbon sequestration is one approach explored in recent years towards preventing global warming and associated impacts. This approach is often initiated in heavy industrial activities, deep coal trenches, coal beds and unmineable coal seams that warrant underground storage techniques in order to reduce the concentration of flue gas and CO_2 emitted to the atmosphere. In a bid to contributing to carbon footprint reduction, particularly in a fast industrializing country like South Africa, subcritical adsorption of two sample coal types; anthracite and bituminous were evaluated from adsorbates of flue gas and pure CO_2. From the results and analysis the following conclusions were reached:

- That since anthracite coal has more potency over bituminous coal, its adsorption capacity was found to be higher than bituminous coal; which is plausibly due to the low ash and high vitrinite contents in sample-A with positive correlation to CO_2 adsorption as against the case of sample-B.
- That both samples were found to have higher attraction for CO_2 as against other gases tested herein i.e., O_2 and N_2; which could possibly be due to the pressure effects the samples were subjected to and also high affinity of the coal types.
- Additionally, from the test conditions set for the study, the results gotten were validated by the outcomes of similar studies carried out by other authors.

In a nutshell, the insistent rise in atmospheric greenhouse gas from industrial and other anthropogenic activities continues to alter the global climate system. These changes have consequential impacts on the health of humans and the environment. As such, drastic and dire measures are required towards curbing the dreadful impacts associated with the warming of the earth's surface by effusion of anthropogenic CO_2. Hence, an optional approach as reported herein to tackle these progressive environmental challenges through sequestration and isolation of CO_2 showed promise. The generated data could therefore, add to the basis for assessing flue gas and pure CO_2 sequestration on South African coals.

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