Modeling of Brick Kilns for the capture of CO_2 from flue gases—A step towards sustainability

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Abstract

Coal and wood are commonly employed in the manufacturing of bricks in Pakistan. The carbon emissions from brick kilns must be controlled for cleaner environment. The objective of this research is the development of a simulation model in order to mitigate carbon emissions from brick kilns. Statistical data of flue gases of a brick furnace has been identified for the removal of carbon dioxide before it enters the environment. Since post-combustion carbon capture technique is widely accepted as the most feasible and economic among all available, a post-combustion carbon technique of Monoethanolamine (MEA) Absorber is employed in our research. This technique has been applied first time in the brick industry of Pakistan. The carbon dioxide recovered can be utilized in the beverage industry and in oil fields, generating profit. This development achieves considerable pollution control and is an important step towards sustainability.

Keywords: Modelling, CO_2 capture, Brick Industry, Sustainable development.

Introduction

Reduction of green house gases (GHGs) has attracted the attention of researchers and scientists around the globe. In recent years, these concerns have become more prominent than ever before. In 1997, the world community including Pakistan accepted the Kyoto Protocol. Its importance and possible implementation was emphasized in 2005. The objective was to address the problem of climate changes occurring due to human activities. Protocols were defined to follow the footwork of UN Framework Convention on Climate Change (UNFCCC) [1]. All the signatories agreed to take legal obligation for the reduction of green house gases by 5.2% of the emissions by 2012. Pakistan has to take actions to fulfill this commitment. Therefore it is obligatory to review and mitigate the greenhouse gases emissions in all industrial sectors including the brick industry.

Besides brick kilns, power plants and automobiles are also contributing to environmental pollution. According to our estimation, there are more than 1000 brick kilns working in the vicinity of Lahore. The annual production of bricks is approximately 46 million per year from more than 6000 brick kilns in Pakistan. It has been estimated that approximately 533019 tons of untreated greenhouse gases are emitted from these kilns on an annual basis which contribute to various environmental problems [2]. Due to insufficient height of kiln chimneys, the smoke returns to the land, ultimately polluting the area.

It is natural for human beings to strive for a better lifestyle with better living conditions. To satisfy this desire, the concept of urbanization appeared. Various activities influence the demand of building materials which include new construction ideas, renovations, congestion of population, and other such technological advancements. In densely populated countries like Pakistan, continuous urbanization and increased buying power of people have played significant roles in increasing production of construction materials like fired clay bricks. Most of the among the 170 million in Pakistan construct houses with the orthodox fired clay bricks, but the problems caused by this method of brick production are deplorably ignored.

During the last fifty years, the brick industry in Europe has gone through a revolution and thousands of small brickworks that existed at the beginning of the 20th century have been replaced by a few hundred large-scale, capital-intensive, highly mechanized brick works. However, the brick industry in rural areas of developing countries like Pakistan, in terms of both brick-making technology and the organization of work, has seen no changes. In villages small-scale brick-making, is organized in family-owned enterprises serving local markets. The traditional technology of hand-molding, sun drying and firing in clamps is still being used.

In this work, we attempt to addressthe need of developing a model to update the Brick Industry manufacturing in a way that the continuous poisoning of environment can be reduced, thereby controlling the amount of CO_2 which is continuously being released into the atmosphere. A model is developed for the capturing of CO_2 which is present heavily among the flue gases emitting from the Brick Kiln.

The process which is commonly used for the production of bricks in Pakistan is shown in Fig. 1. Clay operation, shaping, drying and firing operations are the important steps in the formation of brick as shown in the Fig. 1. Bricks are made from clay, soft slate and calcium silicate with the addition of water to give it a uniform shape.

It starts with the raw clay, preferably in a mix with 25-30% sand to reduce shrinkage. The clay is first ground

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and mixed with water to its desired consistency. The clay is then pressed into steel moulds with a hydraulic press. The shaped clay is then fired at 900-1000 °C to achieve strength [3].

- **Bull's Trench Kilns**

In Pakistan, brick making is classically a manual process. The only type of brick kiln in use is Bull's Trench Kiln (BTK), based on a design developed by a British engineer W. Bull in the late nineteenth century [3].

- **GHG Emissions**

The combustion of coal and wood release carbon dioxide, methane, carbon particle, nitrous oxide and a variety of manufactured chemicals that do not occur in nature like CFCs, ozone, carbon monoxide, non-methane hydrocarbons, (NMHCs) and nitrogen oxides [2].

It is understandable that Pakistan, a country of over 170 million people with one of the highest population growth rates per year, has an ever-rising demand of bricks per year.. Table 1 shows the emissions of GHGs produced by the Brick Industry in all provinces of Pakistan.

Table 1,

CO_2 Emissions of provinces of Pakistan

Province	Provincial Division	Green House Gases Emission (tons/ year)	Green House Gasses Emission %age
Punjab	Total	479467	89.96
Sindh	Total	34332	6.44
Khyber Pakhtunkhwa	Total	14745	2.76
Balochistan	Total	4475	0.84
Grand Total		533019	100

- **Emissions**

The emissions from the Brick Kiln industry in Pakistan is at a frighteningly high level. The values of GHGs release calculated from the up corresponding to 6000 brick units established in the country are 139600, 19600, 495200, 2100, 360, 17 and 540t respectively for total carbon (C), carbon dioxide (CO), carbon dioxide (CO_2), methane CH_4, nitrous oxide (NO), nitrogen dioxide (N_2O) and NO_x. It is evident that GHGs emissions are dominated by carbon dioxide (CO_2) followed by CO and other non- CO_2 gases. Projected contributions of GHGs from the Punjab province to the country's total emissions are highest which can be observed in the Table 1. [2].

- **CO_2 mitigation-A step towards sustainability**

The use of fossil fuels like coal, oil and gas is a major source of CO_2 emissions. This is because use of fossil fuels tends to be economical. In recent years, more than 88% of primary energy in the world has been generated from fossil fuels [4]. Developing countries, like Pakistan, will continue to use relatively inexpensive and abundant coal to meet growing domestic needs of energy. As the demand of bricks is increasing, the use of coal is also greatly increasing. Therefore, coal is expected to dominate Pakistan's GHGs emissions picture in the future. The essence of sustainability is the need to preserve the natural cycles of renewal, that is, a balance between consumption and natural resource recovery. Recovery of CO_2 from flue gases is indeed the first step towards sustainability.

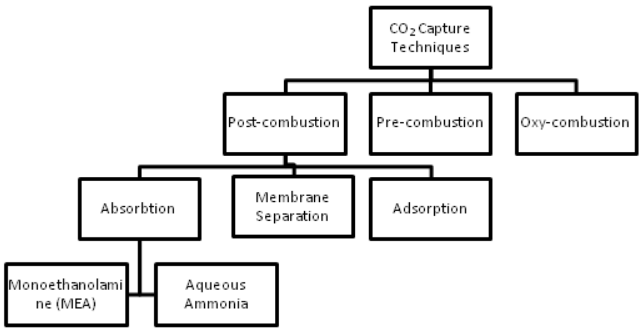

Fig. 2: CO_2 Capture Techniques

Carbon Dioxide Capture Techniques

There are mainly three major routes of capturing carbon dioxide namely (i) Post-combustion (ii) Pre-combustion and (iii) Oxy-combustion as shown in Fig. 2. Post combustion capturing methods involve removal of CO_2 from gases produced by combustion after the combustion reactions. In Pre-combustion methods, CO_2 is absorbed before fuel is burnt. Fuel is first oxidized to produce synthesis gas by the gasification reactions then the water gas shift reaction takes place to form CO_2 concentrated streams and H_2 gas from where CO_2 is absorbed and H_2 is burnt. In oxy-combustion processes, the fuel is burnt with almost pure

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oxygen (95%) and a cryogenic unit is normally used to supply such high purity oxygen [5].

The tree diagram as shown in Fig. 2 illustrates the options for capturing CO_2 with major focus on post-combustion techniques because of retrofit ability of these processes [5].

2.1 Post-combustion Process

Post-combustion process involves removal of CO_2 from the flue gas. Combustion units generate flue gases that are at atmospheric pressure and have CO_2 concentration between 5 to 15%. It has the greatest potential for reducing emissions, because it can be integrated to existing plants which significantly contribute in CO_2 emissions. Some of the methods used for CO_2 capture are disused in the following sections.

2.1.1. Absorption

Absorption processes are being commercially employed to overcome acid gas from natural gas and to remove CO_2 from synthesis gas in the production of hydrogen, ammonia and methanol. CO_2 from brick kilns can be captured by such absorption mechanisms. Various types of amine solutions are being used to scrub CO_2 from natural gas which is an example of CO_2 absorption route.

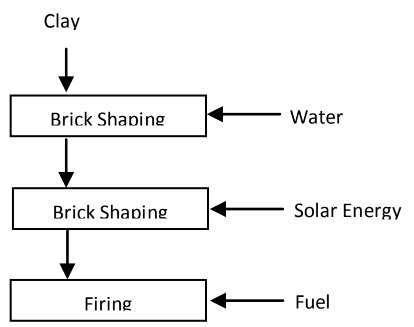


Fig. 1: Brick manufacturing process

CO_2 is absorbed in a solvent and this process is temperature and pressure dependent. Removal of CO_2 by absorption processes is based on the solubility of CO_2 within the solvents. The solubility depends on the partial pressure and on the temperature of the gas. High CO_2 partial pressure and low temperature favor the solubility of CO_2 in the absorbent. The solvents are then regenerated by heating or by reducing pressure.

MEA Solution

Monoethanolamine solution is one of the mainly used solvent for CO_2 absorption. Amines react with CO_2 and form water soluble compounds. Because of this compound formation, amines are able to capture CO_2 from streams with a low CO_2 partial pressure. Amine-based systems, such as Monoethanolamine (MEA), are able to capture CO_2 from the flue gases. This method has been used for years to remove CO_2 from sources of natural gas.

There have been many improvements in amine absorption systems for capture of CO_2, and NO_x from flue gases. It is currently used for comparing other CO_2 capture technologies [6].

3.1.3 Adsorption

Another way of capturing CO_2 is by adsorption route. In this mechanism, the separation relies on the thermodynamic properties of the substance to shift from the gas phase to attach itself to a solid material. This attachment can be physical (physisorption) or chemical (chemisorption). Adsorption encompasses the selective removal of CO_2 from a gas stream to the adsorbents like zeolite or charcoal. This is followed by regeneration (desorption), which is carried out mainly by reducing pressure or by increasing temperature. Sometimes an electric current is also passed through the adsorbent. Some of the adsorbents are washed to separate the attached species [7].

Current status of CO_2 capturing technologies

Systems like Integrated Gasification Combined Cycle (IGCC) and ammonia production are well established processes for CO_2 capture. Solvents used in these processes are effectively separated [6]. The only requirement is that the gas turbines must be capable of using H2-rich fuel. According to latest technological developments MEA Solution, one of the solvents for chemical absorption, is being commercially used for CO_2 capture from flue gases. Other commercially available technologies include CO_2 capture using membranes and cryogenic process [6].

Methodology

MEA Process

Amine solution withdraws carbon dioxide from the flue gas stream. Different amines are used for this purpose. Amines are subdivided into three groups: primary, secondary and tertiary, based on the number of hydrogen atoms attached to the organic group. MEA, diethanolamine and methyldiethanolamine are most commonly used primary, secondary and tertiary amines respectively [8].

MEA is the strongest base of the different amines and so reacts most rapidly with the acid gases. MEA will remove both hydrogen sulfide and CO_2. It is generally considered to be non-selective between these two acid gases. With the lowest molecular weight of the common amines, it has the largest carrying capacity for acid gases on a unit weight or volume basis. This generally means less solution circulation to remove a given amount of acid gases. In addition, MEA is chemically stable, which minimizes solution degradation; it can be separated easily from the acid gas constituents by steam stripping [9].

The Fig. 3 shows a typical flowsheet diagram of an amine absorption process. Flue gas enters the absorber from the bottom to the top through the absorber where it interacts in counter-clock fashion with amine solvent (MEA). Absorbed CO_2 is separated in the stripping unit and the regenerated solvent is re-used in the absorber unit.

Chemical reactions

The absorption of carbon dioxide by MEA solutions involves a complex system of parallel and consecutive reactions in the aqueous phase. The principle reaction is as follows:

$$C_2H_4OHNH_2 + H_2O + CO_2 \rightleftharpoons C_2H_4OHNH_3^+ + HCO_3^- \quad \textbf{(1)}$$

During the absorption process, the reaction proceeds from left to right; during regeneration, the reaction proceeds from right to left. The proposed mechanism of reactions between CO_2 and amines are shown below:

$$CO_2 + MEAH + H_2O \rightleftharpoons MEACOO^- + H_3O^+ \quad \textbf{(2)}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \quad \textbf{(3)}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad \textbf{(4)}$$

$$MEAH + H_3O^+ \rightleftharpoons MEAH_2^{\ +} + H_2O \quad \textbf{(5)}$$

$$MEAH + HCO_3^- \rightleftharpoons MEACOO^- + H_2O \quad \textbf{(6)}$$

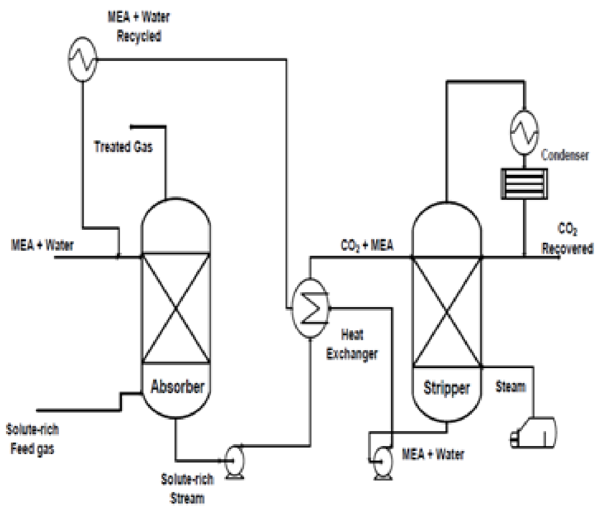
According to this mechanism, the majority of the CO_2 captured will result in the formation of bicarbonate in the liquid amine capture system. In aqueous media, there is a requirement of 2 mol-amine/mol-CO_2 for the formation of stable bicarbonate compounds resulting in the capture of CO_2 [10].

When capturing CO_2 from flue gas, MEA process requires SO_2 to be removed first from the flue gas stream, since MEA is degraded by SO_2 and oxygen, forming irreversible degradation products.

The purpose of this work is to reduce the emission of CO_2 from the selected brick kiln, as this gas is among the major culprits causing green-house effect which has ultimately resulted in drastic and disastrous weather changes and temperature-rise to alarming levels across the globe. Each year the addition of Carbon dioxide solely from the brick industry of Pakistan is 35072.65t. Gas absorption has so far been the most useful and advantageous technique which has been covered well in the section post-carbon techniques.

Table 2.
Flue gas composition from Brick Kiln

Sr. Number	Component	Mole Percentage
1	N_2	71
2	CO_2	6.06
3	CO	3.94
4	NO_2	8.89
5	H_2O	3.11
6	H_2	2.12
7	SO_2	4.88



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Different models and methods have been proposed and tested. In our model, we have chosen MEA as the solvent. The model was developed on HYSYS 7.1. General NRTL was selected as the fluid package. This fluid package is quite versatile and it not only accommodates the properties of our system components but also the aqueous and mixed solvent systems. The flow-sheet of our model is shown in Fig. 3

The temperature of gases emitting from top of the brick kilns is in the range of 120 to 150°C. The composition of the flue gasses were found using industrial combustion and emission analyzer (E8500, USA) which is shown in Table 2. Aqueous MEA solution introduced from top of the column absorbed most of the CO_2 and the treated gas contained almost negligible amount of CO_2. In order to make the process economical, a stripper was installed after the absorber. By the virtue of stripper, not only MEA solution was recovered but also CO_2 was regenerated. The recovered MEA solution was then recycled to the top of the absorber.

In our model as shown in Fig. 3, kinetic and hydrodynamic aspects were also considered so the results of our model depicted realistic values. These values were then compared and verified by the reported values. In order to recover the adsorbate or the solute-gas (CO_2 in our case) and to regenerate the adsorbent or liquid solvent (MEA solution in our case), a stripper was also installed next to the absorber. The stripping was done with steam at low pressure. In our HYSYS model, we varied different parameters (i.e. Temperature, Pressure, Flow-rate, MEA concentration etc.) and examined the resulting percentage of CO_2 absorbed.

While simulating absorber and stripper, special attention was paid to find a workable temperature and pressure range because too high pressure and too low temperature in absorber can lead to condensation of feed gas. Whereas, in stripper, high temperature and low pressure can result in vaporization of liquid feed. The tables and graphs resulting from this simulation of our proposed model are shown in results and discussion section.

Results and Discussion

The rate of absorption is affected by variables such as temperature, pressure, flow-rate, solvent percentage etc. All these variables were manipulated to study their effect on absorption with the help of resulting tables and trends. The results of all these parametric changes are discussed one by one.

Effect of Temperature on CO_2 Absorption:
It is a well known fact that temperature is inversely related to the rate of absorption which agree with the results of our model. The system temperature was varied from 20°C to 50°C and there was a marked decrease in absorption rate with the increasing temperature. The resulting graph is shown in Fig. 4.

It can be seen from Fig. 4 that our model follows standard pattern of increase in absorption with decrease in temperature. Moreover, for better validation of our proposed model, we have completed the simulation using solvents of different flow rates which is clearly depicted in the figure.

Effect of Flow rate on CO_2 Absorption:
The results obtained by simulation of our HYSYS model show agreement with the standard findings that there is increase in absorption with that of increase in flow rate. In our HYSYS model, we used different flow-rates and the results showed that the rate of absorption increased with flow-rate as shown in Fig. 5. At very high flow rate i.e. after 2500 kg mol./hr the effect of flow rate on absorption does not show the same increasing trend. However, the effect of temperature change with simultaneous change in the flow rate do not show significant changes as shown in the Figure . Model with different variation of temperature was simulated but here the simultaneous effect of flow rate with temperate at 20°C and 50°C on absorption of CO_2 have been shown.

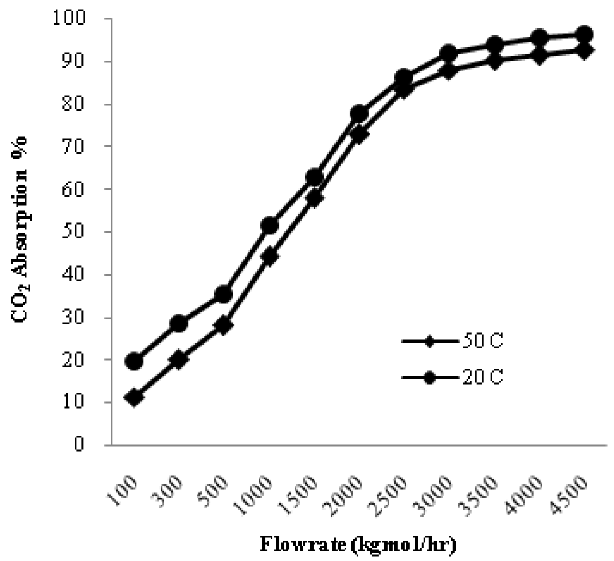

Fig. 5: Effect of Flowrate

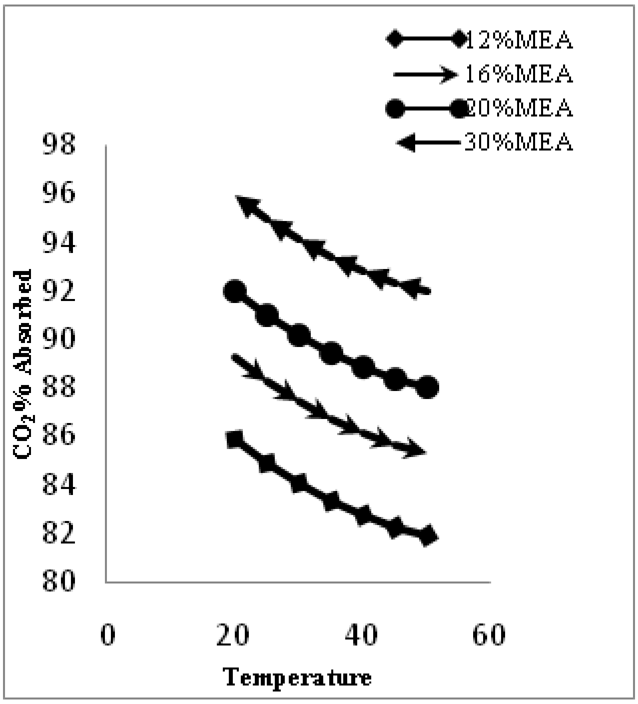

Fig. 4: Effect of Temperature

- **Effect of MEA Percentage on CO_2 Absorption**

The percentage of MEA varied from 10 to 30 %. The HYSYS model showed that the percentage of CO2 absorbed increased with the decreasing MEA percentage. The percentage of CO_2 absorbed increased more rapidly from 10 to 20% but after 20%, the percentage of CO_2 absorbed did not increase with the same rate, which can be seen in Fig. 6. Therefore 20% MEA solution was selected as the optimum solution. The reported values suggested that higher percentage of MEA can lead to corrosion of absorber.

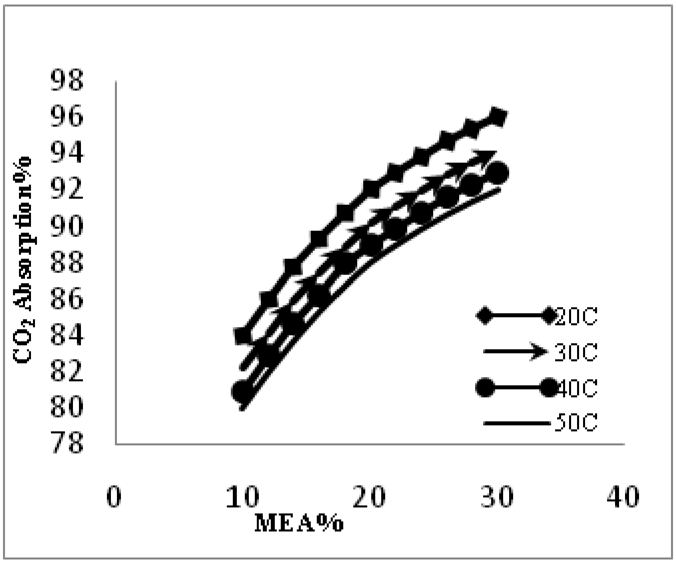

Fig. 6: Effect of Concentration of MEA

Hence, a model with 20 % MEA solution is identified as the best choice. The temperature of MEA solution entering from the top into the absorber is 20^{o}C. The simulation results exhibit that with the use of proposed model from the brick industry in Pakistan, we can save the environment from 35072 tons per year of injection.

As mentioned earlier, the total amount of Flue gases emitting from the Brick Industry is 533019 tons per annum. This means that every year 37311.33 tons of CO_2 is released into the air by only the brick kiln industry. However, if our proposed model is installed throughout the country, only 2238.68 tons/year of C_{O2} will will be released which is shown in the Table 3. The amount of CO_2 captured annually will be 35072.65 tons. This amount of CO_2 could be further utilized to the advantage of industrial processes. These findings are identified for the first time for the Brick industry of Pakistan.

Table 3.

Comparison of Carbon Dioxide emission before and after employing proposed Model

Province	CO_2 at Present (tons/yr)	CO_2 Captured	Green House Gasses Emission %age
Punjab	33562.70	31548.94	2013.76
Sindh	2403.12	2258.93	144.21
Khyber P.	1032.18	970.25	61.93
Balochistan	313.31	294.53	18.78
Total	37311.33	35072.65	2238.68

Conclusion

In this work, a model has been developed and simulated, which aims at the control of CO_2 gas which is continuously entering to the environment from the brick industry in Pakistan. It is for the first time that the brick industry in Pakistan has been analyzed with this perspective and a model is proposed for the mitigation of major GHGs i.e. CO_2. With the implementation of our model, the result showed that 94% of CO_2 emitting from Brick kiln is captured. A solution of 20% MEA has been found to be appropriate for high absorption of CO_2 exhausting from the Brick Kiln with other flue gases. If all the Brick Kilns in Pakistan employ the proposed model, then 2238.68 tons of CO_2 can be captured. Moreover, the proposed model follows the exact trends regarding the absorption of CO_2 dependency with changes in temperature, pressure, and flow rate with that of the reported values in the literature.

In future work the authors plan to carry out the com-

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parison of economic feasibility of proposed work with the idea of the replacement of BTK with Vertical Shaft Brick Kiln (VSBK).

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