REMOVAL OF CO₂ FROM GAS STREAMS IN AIRLIFT REACTORS

BY

PETRONELA COZMA and MARIA GAVRILESCU

Abstract. Emissions of carbon dioxide (CO₂) and other greenhouse gases have become a major environmental issue due to their intensive contribution on the global warming. In the last decades the removal of CO₂ from gas mixtures has become an important industrial operation due to the necessity of different gases purification and from recovery reasons taking into accounts the large applications of CO₂ in chemical and food industry. Various techniques have applied for CO₂ removal. These technologies are based on different physical, chemical or biological processes. In addition several types of contactors have been reported for CO₂ removal such as stirred tanks, packed columns, bubble columns and membrane contactors. This paper discusses the most recent application of airlift reactors in flue gas treatment, in particular the potential of application for the effective CO₂ removal from contaminated flue gases taking into account the most important advantages of these devices: simple design and construction, no moving parts, high mass and heat transfer, intensive mixing, low shear stress to cells, low energy consumption, low operational costs. The most relevant characteristics and properties of CO₂ as well as the most applied technologies for CO₂ removal are reviewed in this paper, based on the information from literature data.

Key words: airlift reactor, absorption, CO₂ removal.

1. Introduction

In the last decades, the emissions of pollutants in the atmosphere have increased considerably with the intensive development of industry processes, transport, electricity, heat production etc. Carbon dioxide (CO₂) is one of the most important greenhouse gases responsible for the intensification of global warming potential and climate change due to its ability to absorb infrared radiation. The increase in atmospheric CO₂ emissions from different industrial emission sources such as combustion of fossil fuels, biological processes...
(decomposition of organic material, fermentation, digestion), manufacture of cement, metallurgical coke, caustic soda etc. lead on the investigation and development of different methods and devices for removing of CO\textsubscript{2} from flue gas streams. In this context airlift reactors are promising contactors that can be successfully applied for removal of CO\textsubscript{2} from contaminated gas streams taking into account the most important advantages of them: simple design and construction, no moving parts, high mass and heat transfer, intensive mixing, low shear stress to cells, low energy consumption, low operational costs [1], [2].

The main objective of this work is to analyze and evaluate the performances of airlift reactors applications in flue gas treatment, in particular the potential for the effective CO\textsubscript{2} removal from contaminated flue gases based on the information from literature data.

2. CO\textsubscript{2} - General Characterization, Properties, Sources

Carbon dioxide is an inorganic compound, colorless and odorless gas, which in solid state is commonly called dry ice. The main chemical and physical properties of CO\textsubscript{2} [3] are related in Table 1. The toxicity and effects of CO\textsubscript{2} on human health can be expressed taking into account its concentration in the air, therefore air with [4], [5]:

- 1% CO\textsubscript{2} can cause drowsiness;
- 5% CO\textsubscript{2} causes dizziness, headaches, confusion and difficulty in breathing;
- 6-10% CO\textsubscript{2} causes headaches, dizziness, sweating and shortness of breath;
- 10-15% CO\textsubscript{2} causes impaired coordination and abrupt muscle contractions;
- 20-30% CO\textsubscript{2} causes loss of consciousness, convulsions and coma;
- > 30% CO\textsubscript{2} can cause death.

Environmental Protection Agency (EPA) of USA classifies the carbon dioxide as a dangerous pollutant that affects human health. Signed in 1997 by 161 countries, the Kyoto Protocol aims to reduce the average amount of greenhouse gases by 5.2% in 2012 compared to 1990. Romania was the first country that ratified the Kyoto Protocol, by the Law no.3/2001 engaged to an 8% reduction in greenhouse gas emissions in the period 2008-2012 compared to 1990.

CO\textsubscript{2} is an important component in the natural carbon cycle (is produced during respiration of animals and plants and in the exchange between the atmosphere and ocean, released in volcanic eruptions and used by plants in photosynthesis). A major source of anthropogenic CO\textsubscript{2} emissions in high concentrations is the biogas resulted from anaerobic digestion of organic waste from the fermentation tanks or landfills, which typically contains 50-80% CH\textsubscript{4} and 20-50% CO\textsubscript{2} and other trace compounds [6]. Also large quantities of CO\textsubscript{2} are released during combustion processes of fossil fuels (oil, gasoline, diesel,
methane, coal). CO$_2$ could have large applications in chemical and food industry. The main applications of carbon dioxide [7], [8] are related in Fig. 1.

### Table 1

<table>
<thead>
<tr>
<th>CO$_2$ Properties [9]</th>
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<tr>
<td>Molecular formula</td>
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![Fig. 1 − The main applications of CO$_2$.](image)

#### 3. Processes and Techniques Applied for Decontamination of CO$_2$ Gas Streams

In the last decades the increase in atmospheric CO$_2$ emissions leads on the investigation and development of different methods and devices for removing of CO$_2$ from flue gas streams. Various techniques have applied for CO$_2$ removal/capture such as [10]:

- physical absorption (scrubbing liquid);
- chemical absorption (chemical reaction with a liquid, such as absorption in aqueous amine);
adsorption in solid sorbents such as activated carbon, zeolites, carbonates;
membrane separation processes;
cryogenic separation processes (high-pressure cooling);
biological methods (biofixation of carbon dioxide by photosynthetic organism).

Among these methods, the *chemical absorption* using aqueous alkanolamine (monoethanolamine, diethanolamine, methyl diethanol amine, 2-amino-2-methyl-1-propanol) or hot potassium carbonate solvents is currently the most promising industrial process for removal of CO$_2$ from different gas streams [11]. In addition several types of gas-liquid contactors have been reported for CO$_2$ removal such as venturi scrubbers, spray tower, stirred tanks, packed columns, bubble columns [10].

Petrov *et al.* [11] studied the chemisorptive removal of carbon dioxide from process streams using a slurry bubble column and a mixture of hexadecylamine or dodecylamine in various concentrations with methanol and others alcohols as the solvent. The conversion rate of CO$_2$ was significant (up to 99% for CO$_2$ absorption with methanol as the solvent). Álvarez *et al.* [12] carried out gas-liquid mass transfer studies of carbon dioxide in polluted aqueous solutions with surface active substances in a cylindrical bubble column. The authors noticed that the flow rate of gas and liquid phases produced an intensive increase of mass transfer rate due to the effect upon the interfacial area or upon driving force.

The conventional column absorbers used for CO$_2$ removal are energy-consuming and are difficult to operate due to the problems associated with foaming, flooding or entrainment [13]. In this context researches have been conducted in order to develop new economical solutions. Studies showed that *membrane gas absorption process* is a good alternative to conventional techniques [13]. For instance, Portugal *et al.* [14] developed a novel efficient technology based on the application of hollow fiber membrane contactors with regenerable liquid absorbents for carbon dioxide removal from anaesthetic closed breathing circuits. The performances of the contactor were analyzed by a 2D numerical model developed by authors.

*Physical absorption* of CO$_2$ involves gas absorption in an absorbing liquid (solvent) under high pressure without chemical reaction. The most physical solvents used for CO$_2$ removal are: water, methanol, selexol (a mixture of dimethyl ether and polyethylene glycol), propylene carbonate, N-formyl morpholine, N-metilpirolidonă, tributyl phosphate, metilcianoacetat. Lampert and Ziebik [15] analyzed the CO$_2$ removal process applied to metallurgical fuel gases: blast-furnace gas and Corex gas using physical absorption process with the Selexol solvent. They obtained a specific power consumption of 335 kJ/kg CO$_2$ and 505 kJ/kg CO$_2$ for Corex gas and Blast furnace gas, respectively. The specific amount of CO$_2$ removed for Corex gas and Blast furnace gas was 0.484
kg $\text{CO}_2/\text{kg}_{\text{fuel}}$ and 0.215 kg $\text{CO}_2/\text{kg}_{\text{fuel}}$, respectively. Also they obtained a purified gas of 5.2% and 1.9% $\text{CO}_2$ for COREX and Blast furnace raw gas containing 35% $\text{CO}_2$ and 16% $\text{CO}_2$, respectively.

Adsorption of gases on solid adsorbents is an efficient technique due to the high adsorption capacity, high selectivity, good mechanical properties and ease regeneration of the adsorbent [16]. Yong et al. [17] investigated the adsorption capacity of carbon dioxide on high surface area carbon-based adsorbents at high temperature. The results showed an adsorption capacity for carbon dioxide of 0.28 and 0.22 mol/g at 300°C and 1 Bar pressure.

Biofixation of carbon dioxide by photosynthetic microorganisms (usually microalgae) is an efficient biological method applied for the capture and storage of $\text{CO}_2$ that has been extensively investigated as an alternative of chemical and physical processes being an economically feasible and environmentally sustainable technology [18]. According to Milne et al. [19] the photosynthetic microorganisms are able to “capture sunlight and use that energy to store carbon in forms useful to humans such as fuels, food additives, and medicines”. The $\text{CO}_2$ removal rates were examined by Jacob-Lopes et al. [20] in a bubble column photobioreactor using a culture of the cyanobacteria *Aphanotoce microscopica* Nägeli. The authors underline the importance of operational parameters (temperature, light intensity, $\text{CO}_2$ concentration) of the photobioreactor on the kinetics of carbon dioxide removal. They observed that the ratios between constant for the rate of carbon dioxide removal as a function of the constant for the rate of carbon dioxide lost to the atmosphere were higher under the conditions of 25°C, 15% of carbon dioxide concentration and independent of the light intensity. Sydney et al. [21] evaluated the amount of the carbon dioxide assimilation of four microalgae: *Dunaliella tertiolecta*, *C. vulgaris*, *Spirulina platensis* and *Botryococcus braunii*. The authors obtained a carbon dioxide fixation rate (mg L$^{-1}$ day$^{-1}$) equal to 251.64 for *C. vulgaris*, 496.98 for *B. braunii*, 318.61 for *S. platensis* and 272.4 for *D. tertiolecta*. Lee et al. [22] studied the $\text{CO}_2$ fixation from concentrated sources such as power plant exhaust using two species of algae *Chlorella sp.* and *Chlorococcum littorale*. The growths of microalgae are influenced by temperature, $\text{CO}_2$ concentration and light intensity. They obtained a maximum grow of *Chlorella sp.* of 0.21 dry cell at 6 Klux light intensities. In the same time the growth of *Chlorella sp.* was influenced by the concentration of $\text{CO}_2$, therefore at concentration of 10% and 20% $\text{CO}_2$ the growth of the algae was not inhibited but was declined to about half at 30% $\text{CO}_2$ concentration. At temperature of 26°C and 30°C the two species showed a maximum growth.

As a conclusion of this section the following aspects must be notice and taken into account in order to choose the optimum method of removing carbon dioxide from contaminated gas streams:
− the main disadvantages of absorption process is that the pollutant is transferred into another phase and the pollution problems still remain because the pollutant is not destroyed [23];
− chemical absorption involves high energy consumption resulting from the chemical reaction and during heating of absorber and is recommended for low gas flow rates and low concentrations of impurities in gas [24];
− biological processes are more effective and more economical methods compared with conventional physical and chemical methods; an important disadvantage of this method is that it can be applied usually for low concentrations of pollutants, higher levels affecting the activity of microorganisms.

4. Application of Airlift Reactors in Gaseous Streams Treatment

Airlift reactors are simple gas-liquid or gas-liquid-solid contactors characterized by pneumatic agitation, specific flow pattern and particular hydrodynamic characteristics that make them more efficient and attractive compared with other devices such as stirred tanks and bubble columns. As a result many applications of airlift reactors may be found in chemical and biotechnological industry for several type of processes (catalytic conversion of hydrocarbons, coal liquefaction, selective oxidation of alcohols, absorption processes, extraction, Fischer-Tropsch synthesis, production of antibiotics, proteins, vitamins, aerobic fermentation, aerobic cultivation, wastewater and flue gas treatment) [25], [26].

Initially airlift reactors were developed for wastewater treatments but these devices showed a significant potential for application in gas separation, purification and waste gas treatment, in particular using biological methods. Biological waste gas treatment in bioreactors is a new treatment alternative for conventional techniques (adsorption, absorption) [23]. The airlift system having a well-distributed and low shear stress creates optimal conditions for cultivation of organisms sensitive to intense shear forces. Therefore, according to Lo and Hwang [27] the airlift system “provided a more advantageous environment for the biological processes”.

A baffled airlift reactor was applied by Ensley and Kurisko [28] for removal of trichloroethylene (TCE) from vapor phase using two species of microorganism: Pseudomonas cepacia or Pseudomonas mendocina. The authors varied TCE concentrations, air flow rates between 100 and 350 mL/min and cosubstrate feed rates. According to their results the concentrations of TCE up to 4,000 µg/liter of inlet air were degraded by at least 90% removal efficiency (RE). Increasing airflow rate leads on the decrease of TCE removal efficiency to about 60%. Zuber [29] compared the performances of an airlift reactor and trickling filter applied for the removal of dichloromethane (DCM) from air, operating with a biocatalyst fixed on sand. The airlift reactor showed a
higher performance (the maximum DCM removed was 2300 g/m$^3$ h) compared with trickling filter (the maximum DCM removed was 450 DCM g/m$^3$·h). A novel airlift bioscrubber configuration was developed by Edwards and Nirmalakhandan [30] for the removal of air phase benzene, toluene and xylene (BTEX) compounds. According to the mathematical model developed by authors for this process, the removal rates higher than 99% can be achieved for benzene and toluene in the air stream with concentrations <1000 ppmv. An airlift inner-loop bioreactor immobilized with Achromobacter sp was applied by Quan et al. [31] for biodegradation of 2,4-dichlorophenol and phenol. The removal efficiency of 2,4-dichlorophenol decreased from 100 to 87.9% with increasing of phenol loading rates while the RE % of phenol were about 99.6%. An airlift bioreactor with biological membrane was applied by Jianping et al. [32] for the removal of ethyl acetate in air streams. Under the optimum operation conditions: temperature of 20–30°C, pH 6.5–7.5 and waste gas influx of 0.05 m$^3$/h, the average removal efficiency of ethyl acetate was higher than 98%. A laboratory and pilot scale new air-lift-tube absorber with recycle and reaction tubes was applied by Bekassy-Molnar et al. [33] for the absorption of sulfur dioxide from SO$_2$/air mixture into sodium citrate buffer solution. The removal efficiency of SO$_2$ was significant (85% for both absorbers). Wang et al. [34] developed a three-dimensional transient computational fluid dynamics (CFD) in order to simulate the biotreatment of toluene waste gas in a laboratory scale airlift reactor. The authors observed that superficial gas velocity influenced significantly the treatment process. Therefore, the RE varied from 88 to 94% at gas phase inlet concentration of 500 mg/m$^3$ and superficial gas velocity variation from 0.01 to 0.02 m/s. At superficial gas velocity value of 0.0075 m/s and variation of gas phase inlet concentration from 500 to 2000 mg/m$^3$, RE was around 93%. These results are available for simulated transient RE. In case of experimental data, the RE obtained was 99%, therefore the model fit well with experimental data.

**CO$_2$ removal in airlift reactors.** In the last decades airlift reactors claimed to be essential for the design and development of a new generation of photobioreactors for cultivation and growth of photosynthesis organism [35]. For instance, Xu et al. [35] designed and developed a simple and low-cost airlift photobioreactor for microalgal mass culture. In a further work, Xu et al. [36] compared the effect of airlift and bubble column photobioreactors on growth and photosynthesis in vegetative gametophytes of U. pinnatifida. As it was expected higher growth rate of microorganism were achieved in airlift reactor compared with bubble column.

Many investigations have been made in order to demonstrate the applicability of airlift photobioreactors in CO$_2$ removal from gas streams. For instance, Yamada et al. [37] cultivated Cyanobacterium anacystis nidulans R2 in an airlift bioreactor in order to study cell-growth characteristics of this strain and its capability for CO$_2$ removal. At concentration of 5% CO$_2$ the highest
growth rate of strain (0.046 h\(^{-1}\)) was achieved. The authors notice that the cell mass concentration was less affected when the CO\(_2\) concentration varied from 5\% at 30\%. Mazzuca Sobczuk et al. [38] obtained a maximum CO\(_2\) uptake efficiency of 63\% by microalga *Phaeodactylum tricornutum* in a tubular airlift photobioreactor. Chiu et al. [39] applied an airlift photobioreactor with a porous centric tube in order to assess biomass production and CO\(_2\) removal using a marine microalga *Chlorella sp*. Under the conditions of 5.15 g/L biomass concentration, 0.125 vvm aeration, aeration gas containing 10\% CO\(_2\), the maximum CO\(_2\) removal efficiency was 63\%. Hincapie et al. [40] designed and developed a novel 30-liter laboratory scale airlift photobioreactor for growing algae that can be further applied for CO\(_2\) remediation in diverse industries. Cultivation of wild mixed microalgae in an airlift photobioreactor was developed by Du et al. [41]. The authors obtaining a better growth rate of microalgae feeding with 10\% CO\(_2\) compared to of that feeding with air. Fan et al. [42] compared the performances of a membrane-photobioreactor applied to remove CO\(_2\) using *Chlorella vulgaris* with other three reactors: draft tube airlift photobioreactor, bubble column and a membrane contactor. The authors obtained a CO\(_2\) fixation in the membrane-photobioreactor of 1.95, 2.15, and 6.40 times higher than that in the other three reactors. However it is important to notice that the membrane photobioreactor was designed based on the airlift reactor construction, replacing the cross- shaped air sparger with a dead-end hollow fiber membrane.

5. Conclusions

Carbon dioxide is one of the most important greenhouse gases responsible for the intensification of global warming potential. Several methods (physical and chemical absorption, adsorption, membrane separation processes, cryogenic separation processes, biological methods) and devices (venturi scrubbers, spray tower, stirred tanks, packed columns, bubble columns, airlift reactors) for removing of CO\(_2\) from flue gas streams are investigated and developed. Chemical absorption using aqueous alkanolamine is currently the most promising industrial process for removal of CO\(_2\) from different gas streams in spite of the disadvantages of the absorption process: the pollutant is transferred in to another phase and the pollution problems still remain because the pollutant is not destroyed. In addition, chemical absorption process involves high energy consumption resulted from the chemical reaction and during heating of absorber and in the same time it is recommended for low gas flow rates and low concentrations of impurities in gas. Biological processes are more effective and more economical methods compared with conventional physical and chemical methods. An important disadvantage of this method is that it can be applied, usually, for low concentrations of pollutants, higher levels affecting the microorganism’s activity.
Airlift reactors have extensively been studied and applied in chemical and biotechnological process as well as in environmental remediation. ALRs showed a significant potential for application in gas separation, purification and waste gas treatment, in particular using biological methods. Numerous applications have been reported for treatment of several flue gas contaminants (toluene, trichloroethylene, BTEX, ethyl acetate, SO₂, 2,4-dichlorophenol and phenol). In addition, ALRs claimed to be essential for the design and development of a new generation of photobioreactors for cultivation and growth of photosynthesis organism for CO₂ removal. Studies are still necessary to be done in order to demonstrate the applicability of these devices for carbon dioxide removal using physical and chemical methods. But it is believed that ALRs are suitable devices for treatment of contaminated CO₂ gas effluents using different physical-chemical and biological methods due to the high efficiency removals of a large class of pollutants from contaminated media.

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Gheorghe Asachi” Technical University of Iaşi, Department of Environmental Engineering and Management

e-mails: petronela_cozma@ch.tuiasi.ro
mgav@ch.tuiasi.ro

REFERENCES


### ÎNDEPĂRTAREA CO₂ DIN FLUXURI GAZOASE CONTAMINATE ÎN REACTOARE GAZ-LIFT

(Rezumat)

Emisiile de dioxid de carbon (CO₂) precum și a altor gaze cu efecte de seră au devenit o problemă majoră de mediu datorită contribuției intensive a acestora asupra fenomenului de încălzire globală. În ultimele decenii îndepărtarea CO₂ din amestecurile de gaze a devenit o problemă industrială importantă datorită necesității purificării diverselor surse de gaze precum și din motive de recuperare având în vedere numeroasele aplicații ale CO₂ în scopuri industriale și alimentare. Pentru îndepărtarea CO₂ din fluxurile gazoase contaminate s-au aplicat diverse tehnologii. Aceste tehnologii au la bază diverse procese fizice, chimice și biologice. În același timp pentru îndepărtarea CO₂ au fost raportate diverse tipuri de contactoare precum: vase cu amestecare, coloane cu unplutură, coloane cu barbotare, reactoare membrană. Lucrarea de față prezintă cele mai recente aplicații ale reactoarelor gaz-lift la tratarea fluxurilor gazoase contaminate, în particular potențialul aplicării la îndepărtarea CO₂ din fluxurile de gaz, având în vedere cele mai importante avantaje ale acestor aparate: proiectare și construcție simplă, lipsa pieselor în mișcare, viteză mari de transfer de masă și căldură, amestecarea intensă a fazelor, forța de forfecare reduse care crează condiții optime de cultivare a unor organismi sensibile la forțe de forfecare intense, consum energetic redus, costuri operaționale scăzute. Pe baza informațiilor din literatura de specialitate lucrarea prezintă o analiză a celor mai relevante caracteristici și proprietăți ale CO₂ precum și a celor mai aplicate tehnologii de îndepărtare a CO₂.