



PLASTICS PYROLYSIS GAS ULTRACLEANING

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Pablo Andres Gangotena Palacios

Examiner(s): Assistant Professor Kristian Melin,

Assistant Professor Nima Rezaei,

VTT Supervisor M.Sc. Ville Nikkanen

ABSTRACT

Lappeenranta–Lahti University of Technology LUT

LUT School of Engineering Science

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Pablo Gangotena

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Assistant Professor Nima Rezaei,

VTT Supervisor M.Sc. Ville Nikkanen

Keywords: Pyrolysis, Gasification, Plastic waste, absorption technologies, carbonate processes, mass transfer efficiency, caustic scrubbing.

Pyrolysis of plastic waste is suggested to produce value-added products such as olefins that can be converted to polymers. However, the gaseous mixture produced from the pyrolysis of plastic waste contains several impurities. Tars are an undesired liquid impurities comprised of hydrocarbons and free carbon that can be removed by oil scrubbing. After tars, the main impurities are the acid gasses, including carbon dioxide and hydrogen sulphide, and alkaline gasses like ammonia. Different absorption technologies for gas removal such as adsorbents, membranes and various scrubbing solvents already reported in the literature are compared and discussed. This master's thesis is focused mainly on carbon dioxide and methane absorption using caustic scrubbers. For low carbon dioxide concentrations in the gas inlet, caustic solvents were found to be more efficient, cost effective and readily available compared to amines and organic solvents. Related aspects of the scrubbing process, including the absorber column type, caustic scrubbing concept and gas-liquid mass transfer theory are also presented.

During the experimental part, a set of two glass bottles was used with a simulated gas comprised of CO₂/N₂ to study the effects of different sodium hydroxide concentrations ranging from 0.12 to 12.77 g/L. High caustic concentrations at room temperature and pressure, proved to be the most effective conditions to reach low carbon dioxide concentrations at the outlet. For the following experiments the caustic concentration was kept constant along with the experiment conditions like gas feed composition, gas flow, temperature and pressure. However, the reaction times that are directly related with the number of bottles were varied from one to six bottles. The best performance was achieved by the six-bottle system, meaning longer residence times and lower ppm concentration of CO₂ at the outlet. With a functional six bottle system it was time to test if organic gasses were absorbed along with CO₂. While the operation parameters remained unchanged, the new inlet gas mixture was composed by CO₂/N₂/CH₄. The experiment was brief, lasting less than an hour, where no absorption of methane was observed. The experimental results will aid in the process design of industrial-sized scrubbing columns.

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Appendix 3. Outlet methane volume percentages obtained in high alkaline concentrations for methane absorption experiment.

1 Introduction

The development of our society and population growth have led to an unregulated production and consumption of plastic goods that increase every year. The absence of governmental and environmental policies to manage a proper plastic waste disposal has resulted in the presence of microplastics and plastic fibrils in different natural ecosystems (Aretoulaki, Ponis, Plakas and Agalianos 2020). The most affected is the marine ecosystem, where wind and surface currents favour the spread of plastic waste through the oceans. Plastics can take hundreds of years to decompose releasing toxic and harmful pollutants into soil and water which can have a negative impact. A common way used technique to prevent plastic decomposition in soil is through landfilling where plastics are buried in an insulating cover. To reduce landfilling there are different valorisation methods that are divided in four main categories. The first category is referred to as in-situ recycling, which involves recycling plastic waste on the site where it was disposed of, often done by individuals. The second category is mechanical recycling or separation, which utilizes more advanced recycling technologies (Beccaria et al., 2023). The third category is related to thermolysis and chemo-lysis processes where the chemical composition of the plastic is altered depending on the needed products. The final category is related to the production of hydrocarbons destined for energy production (Miandad et al., 2016).

For this study we will focus on the third valorisation category related to thermochemical processes, being pyrolysis and gasification commonly used at industrial level (Qureshi et al., 2020a; Salaudeen, Arku and Dutta 2019). Thermochemical processes offer the benefit of increased selectivity towards the intended products, while also minimizing the release of harmful emissions to the environment (Qureshi et al., 2020b). Plastic degradation in pyrolysis starts with a series of arbitrary endothermic chain reactions, resulting in the fragmentation of large polymer chains and the subsequent creation of smaller hydrocarbon chains with diverse properties and weights. The product mixture obtained is comprised of pyrolysis oil, non-hydrocarbon gases and solid char. Pyrolysis oil amounts may vary depending on the initial plastic composition (Sharuddin, Abnisa, Daud and Aroua 2016). Gas composition and quality can be improved by performing cleaning processes, being the most important absorption, adsorption, membrane filtration among others (Simell et al., 2014). Absorption is a commonly employed method for eliminating undesirable gaseous

components. This involves utilizing a non-volatile solvent that is typically distributed over the top of a column. Commonly used solvents for the acid gas scrubbing process are amines (mono-ethanol amine MEA, di-ethanol amine DEA, methyl di-ethanol amine MDEA), organic solvents (methanol, ethanol), sodium hydroxide, potassium carbonate (Scholz, 1995; Shahrak, Ebrahimzadeh and Shahraki 2015; Vo et al., 2018). When there are large amounts of acidic gases present in the feed gas is better to use amines or organic solvents since they can be regenerated by stripping, but they represent extra design and energy costs. Other absorption methods involve membranes and adsorbents. Membranes have high separation efficiencies, low cost and durability but they are not suitable yet for large scale operations due to poor thermal selectivity and chemical stability during absorption (Saufi, Ismail 2004). Adsorbents are solid porous materials that don't generate liquid waste, have low production costs and can be used at low temperatures and pressures but they will not be studied for this thesis (Elvira, Francisco, Víctor and Alberto 2017). For small amounts of acid gas, solvents like sodium hydroxide (NaOH) are preferred but they cannot be regenerated due to its reactivity during the process. Sodium hydroxide is less toxic, expensive and do not degrade during the scrubbing process (Rattanaya et al., 2021). Single stage caustic scrubbers can decrease the amount of unwanted gases down to ppm levels allowing to perform large scale productions under ambient temperature and pressure with low energy costs (Mamrosh, Darryl, McIntush and Fisher 2014; Panza, Belgiorno 2010; Shahrak, Ebrahimzadeh and Shahraki 2015). For this experimentation the caustic scrubbing process is analysed in a small scale to determine the best CO₂ removal conditions.

This master thesis is structured as following; after introduction comes background and theory, where the plastic waste situation, thermochemical processes to transform plastics into gas and different gas cleaning methods available at the market are explained. The next section is theory and background on caustic scrubbing, where all the theory related to mass transfer in absorption columns is presented. The following section is materials and methods, where the materials used for the experiments and the setup for the absorption system is explained. The next section is results and discussion, where the experimental results are presented with the respective explanation. The last section is the conclusion of all the work done in this thesis.

2 Background and theory

2.1 Plastic waste status

Plastics are versatile and low-cost materials that contribute to the growing demand of our society (Almeida, Marques 2016). Over 8300 million tons were produced from 1950 to 2015 and over the years the plastic production have increased reaching up to 400 million tons in 2020 (Qu et al., 2023; Xu, Q., Xiang and Ko 2020) . The packaging and construction sector account from 17% to 30% of the total plastic consumption, along with other industries that account less but still important amounts (Aretoulaki, Ponis, Plakas and Agalianos 2020). The average lifespan of 40% of the overall plastic produced in the world is about one month (Miandad et al., 2017; Williams, Williams 1997). Plastic waste is separated in post-industrial plastics (clean plastic) and post-consumer plastics (used and discarded plastic) which are classified and explained in Table 1.

Table 1. Plastic types and properties (Miandad et al., 2016; Sharuddin, Abnisa, Daud and Aroua 2016)

Polyethylene terephthalate (PET)	Used for packing and beverages, it has light weight, pressure resistance properties, low volatile material content and tends to lose more aliphatic than aromatic compounds.
High density polyethylene (HDPE)	Used for detergent bottles, oil containers and toys, it is a strong resistant and durable plastic, and it contributes about 17.6% of the total MSW.
Low density polyethylene (LDPE)	Have low tensile strength, good water resistance and are the second largest plastic waste after PP.
Polypropylene (PP)	Has good chemical and heat resistance, does not melt below 160°C and is less dense than HDPE.
Polyvinyl chloride (PVC)	Fire resistant material good for electrical isolation, it is not a recommended plastic to feed in the pyrolysis

	process since it contains chlorinated compounds that lead to hydrochloric acid formation.
Polystyrene (PS)	Has good heat resilience, is durable, strong, light weighted and degrades into a viscous dark colour oil.

Polyethylene, polypropylene, polyvinyl chloride, polyurethane, polyethylene terephthalate, polycarbonate and polystyrene make up 80% of the overall plastic usage (Miandad et al., 2017; Qu et al., 2023).

The main reasons that lead to a proper waste management are public health, environmental protection, value of waste and institutional responsibility issues (Mwanza, Mbohwa 2017). According to the world economic forum related to environmental protection, a minimum of 8 million tons of plastics are dropped in the ocean every year. It has been predicted that by 2030 the plastic amount will increase up to 300 million tons (Aretoulaki, Ponis, Plakas and Agalianos 2020; Syberg et al., 2022). Plastics can last for long time periods since their decomposition process depends on conditions like sun, light, air, water and climate. Long term contact with oxygen and heat cause colour change, cracks and molecular changes, releasing harmful chemical compounds during the process (Qureshi et al., 2020a). Among the release compounds during the process, we have styrene, benzene and heavy metals like Pb, Cr or Cd, which can damage lungs, nervous system and reproductive organs in humans (Xu, Q., Xiang and Ko 2020). The plastics that are not landfilled or discarded in the ocean are incinerated in the open, producing hazardous gases like dioxins, furans and acid gases.

To overcome this problem a recycling conscience with different valorisation methods for plastic treatment can be applied. Mechanical separation techniques like grinding, washing and extrusion, account 20% of the total recycled plastic waste (Miandad et al., 2016). Mechanical processes are difficult and expensive to perform when the plastic waste is mixed with external contaminants like labels, food leftovers, dirt, soil and chemical additives such as colourants, stabilizers, fillers and lubricants (Kremer et al., 2021). Plastic waste contains different types of plastics, each with different polymer chain lengths, making difficult to determine the exact composition of the feed stream (Williams, Williams 1997).

2.1.1 Gasification

Gasification is one of the oldest thermal conversion procedures, developed as a reliable process to substitute fossil fuels. It can be described as a thermochemical process where solid based fuel like carbon, biomass or municipal waste is converted to synthesis gas in the presence of a gasifying medium. Gasification performance will depend directly on the kind of feedstock, reactor type, gasifying medium and operating conditions.

Due to plastic waste nature of viscosity and stickiness, it is a good option to consider a fluidized bed gasifier, since it allows higher throughputs, better gas-solid reactions, good mixing environment, better char conversion and high calorific value of the produced gases (Lazzarotto et al., 2020). The fluidizing design of the reactor allow the hot solid particles inside to behave like a fluid flow, avoiding the formation of cold spots. The operating conditions are related with the gasification medium used, that can be steam, air or pure oxygen. When the temperature of the reactor raises, then there is an increase in the mole fraction of hydrogen and carbon monoxide, followed by a reduction in gases like carbon dioxide, methane and water, in Table 2 there are the main gas products obtained from gasification. There is a similar behaviour when the steam-feed ratio increases in 1.25 (Saebea, Ruengrit, Arpornwichanop and Patcharavorachot 2020).

Table 2. Gas products obtained from air gasification in fluidized bed reactor (Block et al., 2019; Salaudeen, Arku and Dutta 2019).

Feedstock	Temperature	Gas composition vol%				
Plastic waste	700-900 °C	H ₂	CO	CO ₂	CH ₄	C ₂ -C ₄
		14.9-27.9	9.4-18.4	2.7-5	3.8-6.5	2-9

When steam is used as gasifying medium, then the reaction that takes place is endothermic, requiring a higher consumption of energy to maintain the gasifier in the operational temperature (Dogu et al., 2021).

2.1.2 Pyrolysis

Unlike gasification, pyrolysis is a thermochemical process where complex cracking endothermic and exothermic reactions take place, however pyrolysis process has an endothermic nature. Pyrolysis is performed in an atmosphere with no oxygen and temperatures can rank from 350 to 900 °C, depending if it is a slow, fast or flash process (Oasmaa, Lehto, Solantausta and Kallio 2021).

During the reaction the hydrocarbons of large polymer chain that constitute plastic waste break and turn into smaller chain compounds comprised by a general mixture of hydrogen, carbon dioxide, carbon monoxide, hydrocarbon rich gas, char, and oil or wax (Miandad et al., 2017). The end hydrocarbon products variate depending on the composition of the plastic feedstock, for example if in the plastic waste feedstock there are high amounts of polypropylene, then the end product will be mostly iso-olefins, diolefins and only small amounts of paraffins, aromatics and olefins (Beccaria et al., 2023; Kusenberg et al., 2022). Operating conditions like reactor temperature, residence time, heating rates, water presence, toxic elements and catalyst usage can affect the compositions of the final oil, gas and char produced as shown in Table 3 (Miandad et al., 2016). Municipal plastic waste is dirty and mixed with impurities that contain metals with catalytic activity like aluminium, copper or silicon, favouring the production of oil and gas products. It can also contain oxygenated compounds, increasing the production of carbon oxides like carbon monoxide and carbon dioxide (Kusenberg et al., 2022). The hot raw gases leaving the system are often at 900°C, so they get cooled down to 500°C for further tar and hydrocarbon gas reforming (Kurkela, Kurkela and Hiltunen 2016). For this research, we will focus on carbon dioxide, hydrogen sulphide and ethylene.

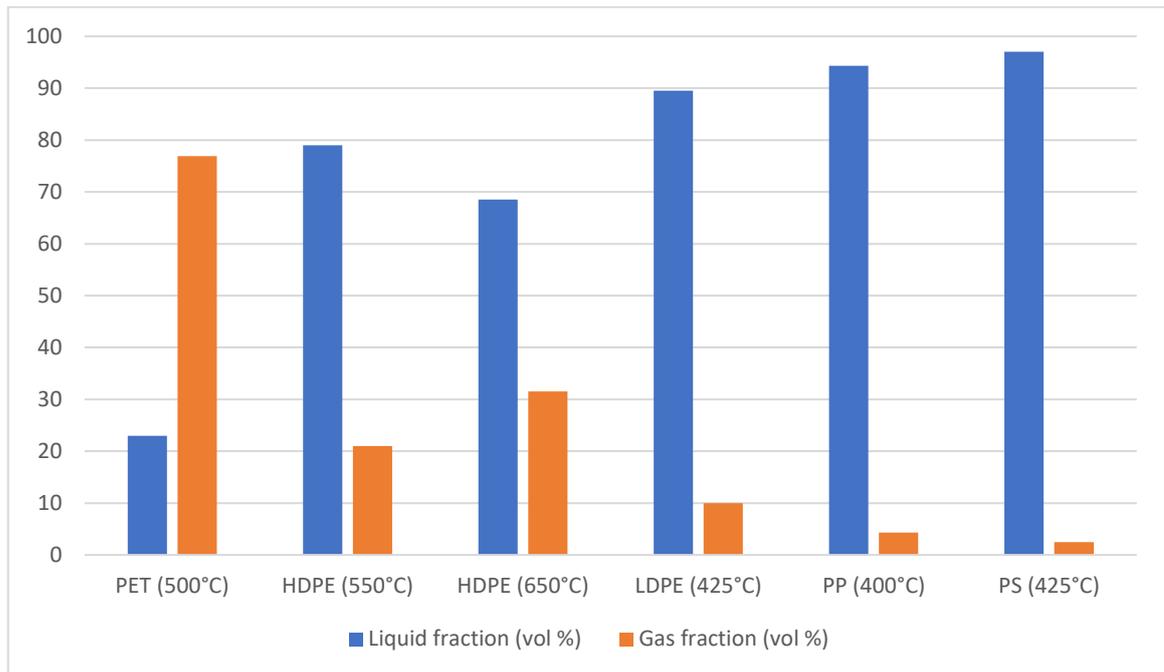


Figure 1. Plastic pyrolysis liquid oil and gas product fractions at temperatures ranging from 400-650 °C (Sharuddin et al., 2016)

Reactions driven at high temperatures 800-900 °C result in a decrease in char and tar formation, leading to more thermodynamically stable products and content of flammable gases like hydrogen, methane, acetylene and aromatics (Almeida, Marques 2016).

Table 3. Plastic waste pyrolysis gas composition at different temperatures (Kaminsky, Kim 1999)

Gas compounds	Volume %	Temperatures				
		685 °C	710 °C	716 °C	738 °C	730 °C
H ₂	vol%	0.4	0.5	0.6	0.7	0.4
O ₂	vol%	0.1	0.3	0.01	0.01	0.01
N ₂	vol%	0.02	0.1	0.01	0.01	0.01
CH ₄	vol%	10.9	12.3	16.2	20.5	11.9
CO	vol%	4.6	5.5	6	1.3	1.3
CO ₂	vol%	2	2.5	1.7	0.6	0.4
C ₂ H ₄	vol%	8.6	8.9	10.1	10.3	8.9
C ₂ H ₆	vol%	4	3.9	3.3	2.2	3.9
C ₃	vol%	0.6	0.5	0.5	0.5	1.2
Propane		0.5	0.6	0.2	0.1	0.6
Propene		6.3	6	3.2	1	5
Butane		0.08	0.08	0.05	0.19	0.03
C ₅ -C ₇	vol%	5.7	4.9	2.2	0.7	3.1

Diolefins / e.g., 1,3 butadiene	ppm	0.8	0.9	0.7	0.5	0.7
Benzene	vol%	9.5	10.8	14	17.4	9.1
Toluene		6.7	6.1	4.8	3.9	7.6
Xylene		0.6	0.6	0.5	0.2	0.8
Styrene	ppb	9	7.9	6.8	8.7	10.8
Napthalene		0.8	1.2	4.2	7.2	2.3
H ₂ S	ppm	-	240	240	-	-
HCl	mg/m ³	-	4	4	-	-
Ethylbenzene		0.9	1	0.9	0.2	2.5
Methylstyrene	ppm	1.4	1.1	1.5	0.2	1.6
Indene	ppm	0.6	0.8	2.1	2.5	1.2
Methynapthalenes	ppm	0.3	0.4	0.5	0.1	1
Butene	ppm	2.1	2.3	0.7	0.1	1.6
Trans-2-butene	ppm	0.2	0.2	0.1	0.1	0.2
Cis-2-butene	ppm	0.2	0.2	0.1	0.1	0.1
C ₇ -C ₉	ppm	2.3	1.6	0.5	0.2	0.5
Methylindene	ppm	0.4	0.3	0.5	0.3	0.7
Diphenyl	ppm	0.1	0.1	0.2	0.1	0.4
Fluorene	ppm	0.04	0.07	0.05	0.18	0.1
Anthracene	ppm	0.01	0.02	0.04	0.63	0.2

2.2 Purification of gas products from pyrolysis of plastic waste

To remove unwanted gasses there are different absorption techniques that are growing popularity in the industrial sector. Solvent absorption, vacuum pressure swing absorption, cryogenic distillation and membrane separation are highly known due to their efficiency for gas absorption (Zhang, Z., Chen, Rezakazemi, Zhang, Lu, Chang and Quan 2018). In order to perform a purification process, it is important to know all the compositions of the pollutant types present in the gas stream and once the information is gathered, then define the most suitable absorption technique (Rezakazemi, Heydari and Zhang 2017).

2.2.1 Membrane absorption

Membrane gas absorption is a known physical separation method which combines the advantages of chemical absorption and membranes (Ibrahim, El-Naas, Zhang and Van der

Bruggen 2018; Zhang, Z., Chen, Rezakazemi, Zhang, Lu, Chang and Quan 2018). Membrane processes are useful to avoid packed bed columns problems such as flooding, foam production, channelling or flow entrainment (Ibrahim, El-Naas, Zhang and Van der Bruggen 2018). Separation is achieved by differential permeation of the components when they cross through the membrane. The structure and small size play an important role, since they allow an individual absorption control on gas and liquid phases (Zhang, Z., Chen, Rezakazemi, Zhang, Lu, Chang and Quan 2018). Membranes have low weight, small volume size, high surface area and low process instalment costs (Ibrahim, El-Naas, Zhang and Van der Bruggen 2018). They are selective about the desired acid gas to be absorbed but it will depend on the absorbent liquid being used. A higher selectivity causes low permeability so the flow going through the membrane must be low to achieve the desired final concentrations (Ibrahim, El-Naas, Zhang and Van der Bruggen 2018). Common solvents that are used in membrane separation systems are sodium hydroxide, sodium carbonate or amine solutions (Zhang, Z., Chen, Rezakazemi, Zhang, Lu, Chang and Quan 2018). Even though membranes are a promising technology, factors like high mass transfer resistance, low membrane lifetime period and wetting affect the purity levels obtained at the outlet, which are not enough to satisfy the proposed environmental standards (Xu, J. et al., 2018). Membranes are susceptible to variables like temperature, pressure, flow and pore size, which must be between 21-25 nm for gas separation (Pandey, Chauhan 2001). The main process is driven through these pores and to get the highest mass transfer coefficient the gas phase should fill the pores completely. When the morphology of the membrane is known, then we can overcome problems related to wetting (Ibrahim, El-Naas, Zhang and Van der Bruggen 2018). In natural gas cleaning processes, its necessary to reduce the hydrogen sulphide concentrations down to 5 ppm which cannot be achieved by using only membranes. To reach those levels it is important to use a hybrid system which combines membrane absorption and amine scrubbing in one stage. Amine scrubbing alone can be energy intensive and represent high capital costs at small gas flows, but in a hybrid system the capital and operating cost of the process decrease, making it suitable to be used at an industrial level (Rezakazemi, Heydari and Zhang 2017). Other option to improve mass transfer in membranes is through nanoparticles. The diffusion properties in nanofluids improve gradually and the absorption rates can increase up to 76% of acid gases (Rezakazemi, Darabi, Soroush and Mesbah 2019).

2.2.2 Adsorption

Adsorption is a heterogeneous process where a solid sorbent interacts with the gas molecules and captures them in a porous structure under determined temperature and pressure conditions (Aaron, Tsouris 2005). Solid adsorbents are cheap to produce, have a high acid gas adsorption capacity, are easy to regenerate with low energy consumption, have good selectivity, fast adsorption rates and are optimal for a cycle production process. The most promising technologies for CO₂ adsorption are PSA (pressure swing adsorption) and TSA (temperature swing adsorption), both using activated carbon at high pressures as adsorbent (Jribi et al., 2017). By using PSA technologies, the power consumption can decrease up to 57% (Wang et al., 2022). Activated carbon is generated by a two-step or a single step process involving pyrolysis (Guo et al., 2020). It can capture vast amounts of sulphur components due to its amorphous structure and microporosity (Frilund, Hiltunen and Simell 2021). Other porous materials available at the market are zeolites, metal oxide sieves, aluminophosphates, activated alumina, silica gel, carbon nanotubes and polymers resins. Zeolites and activated carbons are considered more important, due to their efficiency to capture acid gases. To improve acid gas removal the activated carbon is impregnated with alkaline materials such as NaOH or KOH. Impregnated carbons can achieve high efficiency and fast reaction rates (Yan, Liang, Tsen and Tay 2002). A drawback from the process is that the sorbent cannot be selective, so other gasses similar or smaller than the CO₂ molecule can be adsorbed (Aaron, Tsouris 2005).

2.2.3 Scrubbing

Oil Scrubber:

Tar is an organic contaminant product obtained from pyrolysis. It is comprised by different aromatic carbons that are classified under the category of gravimetric or light (Tarnpradab, Unyaphan, Takahashi and Yoshikawa 2017). Tar is unwanted as a product since it tends to crack, polymerize or condense in the filter or piping systems at temperatures below 350 °C (Unyaphan, Tarnpradab, Takahashi and Yoshikawa 2017). It can clog engine components and pipelines leading to additional expenses in maintenance (Thapa et al., 2019). If released

to the environment these volatile organic compounds can react with nitrogen producing ozone or carcinogenic products (Hariz et al., 2017).

To improve the quality of the product gas obtained after pyrolysis we need to set an upgrading process to remove tars (Zhang, J., Chen, He, He and Hong 2020). Commonly used technologies are elimination and recovery. Elimination is useful when the tar amounts are low but when concentrations are high, then we need to change the state of tar from gas to a condensate phase through a recovery process (Hariz et al., 2017). Tar removal can be achieved at the gasification-pyrolysis temperature or by performing dry and wet removal processes. In wet removal processes water is usually the most common solvent to be used but only with certain kind of compounds. Wet removal takes place at low temperatures with no need of a catalyst, obtaining high tar removal rates (Tarnpradab, Unyaphan, Takahashi and Yoshikawa 2017). Wet scrubbing technologies are performed using packed bed scrubbers, venturi scrubbers and spray towers. Water scrubbing techniques can only absorb 30% of tar but other solvents like natural oil has proven to have higher absorption rates. Oil molecular structure allows to improve dilution of hydrophobic and hydrophilic tars (Tarnpradab, Unyaphan, Takahashi and Yoshikawa 2017). By using canola oil, the tar removal efficiency can go up to 98 wt.%. Scrubbing techniques, used widely to remove volatile compounds, since they promote liquid-gas mass transfer in a column filled with packing material (Hariz et al., 2017). After the absorption tar and oil is separated by centrifugal sedimentation processes or by cooling the oil with a heat exchanger and then bubbling the gas (Thapa et al., 2019). OLGA is a big scale absorption technology for tar, with removal efficiencies that can reach up to 99% by using canola and soybean oils. Many kinds of oils like diesel oil, biodiesel oil, vegetable oil and engine oil have been evaluated. Vegetable oils have a big capacity of tar removal, but they get easily polluted so they must be constantly renewed (Zhang, J., Chen, He, He and Hong 2020)

Amine scrubbers:

Amines are the product of the substitution of a hydrogen atom in an ammonia molecule with a hydrocarbon molecule. They are classified depending on the number of hydrogen atoms present in the nitrogen atom and have names as primary, secondary, or tertiary. Amines have high capacities of absorption and recyclability, making them suitable for acid gas scrubbing

processes (Meng et al., 2022). Amine scrubbing is a wet decarbonization process that was introduced in the year 1930. It was used mainly for acid gas decontamination of industrial scale products like biogas, natural gas and coal-based gas (Meng et al., 2022). This process was attractive to industries due to their fast reaction rates, low viscosity and volatility, good energy performance, resistance to thermal degradation, simplicity, and maturity (Gao, T., Selinger and Rochelle 2019). Amines occupy about 60% of the total market of carbon capture processes, being MEA, DEA, MDEA and DIPA the most common solvents (Chen, L., Huang and Yang 2001). In industrial plants the best solvent is MEA (monoethanol-amine) since it is a cheap solvent that can be found easily in the market (Krótki et al., 2020). MEA can suffer from oxidation and thermal degradation, increasing the amount of solvent and costs. To decrease the regeneration energy of the solvent there are different efficient methods that include absorber intercooling systems and different arrangements for the stripping section (Chung, Wonseok, Roh and Lee 2018; Chung, Wonsuk, Lee 2020). Other alternative is to replace or mix MEA with other amines like AMP, PZ AEEA, EAP, etc. (Krótki et al., 2020). When amines are mixed, they become better absorbents with netter regeneration properties. Usually, the mixtures are between two primary amines or secondary amines with tertiary amines. By mixing MEA with MDEA the absorption efficiency decreases a little compared to only using MEA, but the regeneration efficiency of the mixture improves, reducing energy costs (Meng et al., 2022; Rattanaya et al., 2021).

A negative aspect in the application of amines is the evaporation of water from the desorption tower which carries an important amount of amines, the absorption reaction usually takes place between 25-45°C and the temperature for the stripping area is at 90-130°C. The operating conditions are adjusted according to the flowrate and the target of the final gas concentration (Meng et al., 2022).

Rectisol scrubbers:

Rectisol scrubbing is a physical absorption method with high selectivity for acid gases while separating basic gases like ammonia (Gao, H., Zhou, Luo and Liang 2018). The process uses organic solvents that can operate below the water freezing point to improve selectivity, low freezing points, chemical stability and unlimited solubility. The solubility of CO₂ in an organic solvent like methanol at room temperature is five times higher than water (Chen, W., Chen and Hung 2013). Using methanol as solvent allows to work with low viscosities, low temperatures and enhances the removal of the acid components at moderate partial

pressures and low residence times (Yang, Zhang and Song 2022). Methanol has high thermal and chemical stability at low temperatures causing less corrosion and degradation (Gao, H., Zhou, Luo and Liang 2018). Rectisol process is comprised by two sections, first the scrubbing section where the sour gases are removed and second the stripping section where methanol is recovered. In the stripping section, sour gases like carbon dioxide are recovered and stored for further reactions like chemical liquefaction or carbonation of beverages (Gao, H., Zhou, Luo and Liang 2018). The operating temperatures for the Rectisol process are between 30 to 80 atmospheres of pressure and temperatures that range from 213 to 263 K respectively. After the CO₂ is captured by Rectisol the temperature of methanol must be decreased to improve the gas separation, leading to high expenses related to energy consumption for the cooling process (Chen, W., Chen and Hung 2013). Today there are more than 150 Rectisol plants worldwide with the main goal of recovering most of the spent solvent and the recovery of carbon dioxide in the stripping section (Yang, Zhang and Song 2022).

Caustic scrubber:

Caustic scrubbing is the main scrubbing process taking place in this thesis and it will be focused on acid gas H₂S and CO₂ removal. Caustic scrubbing processes are commonly used in the gas and petroleum refineries to remove hydrogen sulphide, mercaptans and naphthenic acids (Roudsari, Soltani, Seyedin and Chen 2017). Hydrogen sulphide (H₂S) is a colourless, poisonous, flammable and highly toxic sulphur component with odour of rotten eggs (Mamrosh, Darryl, McIntush and Fisher 2014). It must be removed since sulphur compounds can deactivate catalysts and cause unwanted secondary reaction in further gas cleaning steps. It can be detected by humans at concentrations of 0.4 ppb with maximum exposure concentrations of 10 ppm for prolonged periods and 50 ppm for 10 minutes, after this it can start affecting the nervous and respiratory system (Chen, L., Huang and Yang 2001; Panza, Belgiorio 2010). When operating the caustic scrubber, low temperature operations are preferred since H₂S reduction improves and corrosivity decreases (Mamrosh, D. L., Fisher and Beitler 2012). At the gas-liquid mass transfer interphase, hydrogen sulphide diffuses into the solvent NaOH causing a reaction that produces sodium hydrosulphide (NaHS) and water. NaHS can be sold to the paper, tanning or mining industries depending on the purity (Shahrak, Ebrahimzadeh and Shahraki 2015). If the caustic concentration is high meaning

NaOH is in excess, the produced NaHS will react with NaOH to produce sodium sulphide (Na_2S) and water.

To improve the remotion process, we must consider that hydrogen sulphide is a reducing gas and when dissociated its products can be oxidized and removed from the dissociation equilibrium by irreversible reactions. The oxidation reaction takes place first instead of the reaction with carbon dioxide, minimizing the carbonate solids production (Krischan, Makaruk and Harasek 2012). In the reaction the HS^- ions oxidize to elemental sulphur which then reacts with two equivalents of hydrogen peroxide to form sulphite that can be oxidized to sulphate (Krischan, Makaruk and Harasek 2012). When the concentration of the oxidizing agent is low then the equation $\text{HS}^- + \text{H}_2\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O} + \text{OH}^-$ is predominant and elemental sulphur is created as a main product. Elemental sulphur precipitate into solids that are not soluble in water mixtures. If the concentration of the oxidizing agent increases then the main products will be sulphite and sulphate (Krischan, Makaruk and Harasek 2012).

The most important gas used for all the experimental procedures developed in this work is carbon dioxide. It is a colourless and odourless gas formed during the pyrolysis process due to the oxygen present in plastic waste. The reaction between carbon dioxide and sodium hydroxide in excess produces solid sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_3) salts that can form precipitates and be risk for potential fouling and plugging in the system (Mamrosh, Darryl, McIntush and Fisher 2014). Precipitates form faster at low pH values and low temperatures. Elevated temperatures can decrease the absorption rate due to an increase in the partial pressure of the acid gases limited by the equilibria. Gas residence time was more dominant on acid gas removal than the effect of the gas velocity so a residence time equal or above 3 seconds was the optimum (Üresin et al., 2015). There has been many studies oriented to reduce the formation of carbonate salts in the scrubber by reducing the residence time of the gas in the caustic solution. Carbon dioxide require longer residence times to react compared to hydrogen sulphide since it goes through a slow hydrolysing step given by the equation $\text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3 + \text{H}_2$, so a higher selectivity can be achieved for hydrogen sulphide (Krischan, Makaruk and Harasek 2012).

The solubilities of the salts produced from H_2S and CO_2 are different in composition and difficult to remove (Mamrosh, Darryl, McIntush and Fisher 2014). Salts precipitation can be predicted based on solution pH, temperature, CO_2 absorption and NaOH concentration in caustic feed. If there is a higher presence of carbonates in the gas, it's better to maintain the

solution in the basic region to stop the formation of sodium bicarbonate salts. High pH values in the solution and in the feed decrease the solubility of sodium sulphide, but unlike bicarbonate, a higher temperature can help prevent solid sodium sulphide formation. Carbonate and sulphide salts precipitation can occur above the freezing point of water (Mamrosh, D. L., Fisher and Beitler 2012). For big amounts of carbon dioxide and hydrogen sulphide its preferred to perform absorption in an aqueous solution. When the initial gas feed increases in the column the amount of carbon dioxide and hydrogen sulphide removed decreases due to the low residence times in the column. If the pressure increases inside the column then the removal of the acid components increases (Kulkarni, Ghanegaonkar 2019). The spent caustic from the process is disposed for further air oxidation treatment to analyse the different components that got dissolved in the solvent (Copa, Momont and Beula 2021).

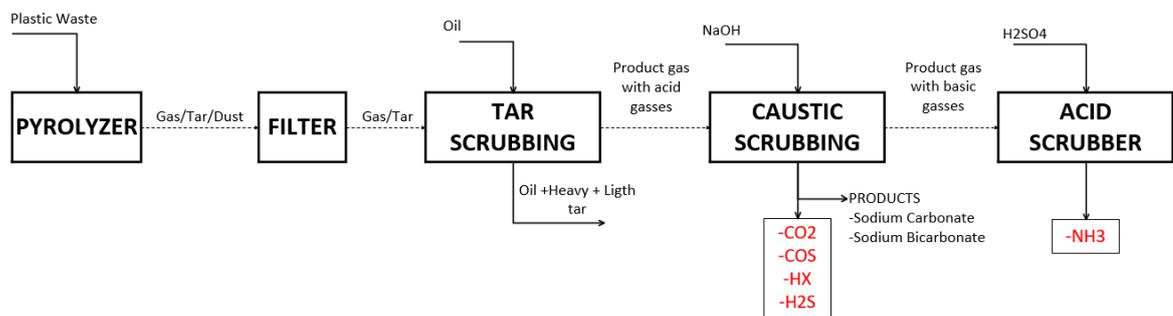


Figure 2. Block diagram for pyrolysis of plastic waste and pyrolysis gas purification using oil, caustic and acid scrubbing.

Acid scrubbers:

Ammonia is an alkaline gas that cause corrosion, decrease the lifetime of the absorption column, poison catalysts and don't allow the fuel gas to be used in gas cells or fuel cells (Üresin et al., 2015). Ammonia can be removed using an acid scrubbing system which is highly efficient, has low water consumption and low waste generation (Cao et al., 2022). The system requires a packed bed column filled with highly porous inorganic packing material that have high void volume and large surface area. Acid solvent is sprayed on top of the packed bed and the contaminated air is introduced horizontally at the bottom so there is always an intensive contact between gas and liquid. The rate of mass transfer is proportional to the concentration gradient between gas phase and liquid phase. The acid solvent in the column must be kept at a pH below 4 to achieve better (Melse, Ogink 2005).

Ammonia is very reactive with strong acids and very soluble in water at low temperatures. Sulfuric acid is commonly used due to its efficiency, low costs, availability, and high market demand for ammonium sulphate. Ammonium sulphate is a side product formed after the reaction between ammonia and sulfuric acid takes place. It can be crystallized to be used as fertilizer where the ratio between kg of sulphuric acid and kg fertilizer is 1.63, being the highest compared to other acidic solvents like citric or acetic acid (Jamaludin, Rollings-Scattergood, Lutes and Vaneekhaute 2018). Sulfuric acid is a strong acid that can cause environmental problems and corrosion in the equipment. Nitric acid was proposed as an alternative, but it turned out to be more hazardous than sulfuric acid due to the oxidizing capability of nitrate ions and the product ammonium nitrate is highly reactive and explosive. By using nitric acid, the scrubbing costs doubled compared to sulfuric acid, the annual cost of using citric or nitric acid instead of sulfuric will represent an increase of 20% of the final costs.

In the column operation with sulphuric acid the absorption of ammonia was about 90% with low operating temperatures that ranked from 15-18°C, but when the temperatures increased to forty Celsius, the absorption dropped to 70%. Other advantage is that sulphuric acid consumes in half of the amount compared to citric and acetic acids because it is a strong diprotic acid with a double concentration of hydrogen ions that will bond with ammonia (Jamaludin, Rollings-Scattergood, Lutes and Vaneekhaute 2018). Ammonia absorption decreases when the pH levels start to increase, high pH led to the conversion of NH_4^+ to NH_3 . The efficiency of removal at pH 4 and 1.7 seconds of residence time was about 84%, no different with a pH of 1.5 at the same residence time (Melse, Ogink 2005)

During the scrubbing process low amounts of N_2O and CH_4 and other organic volatile components such as butanol, butyraldehyde, methylethylketone can be absorbed, achieving removal efficiencies of 90% of butanol and 30% of butyraldehyde in 20 milliseconds. The removal of volatile organic compounds is independent of the pH of the solution, most of them don't have alkaline or acidic properties and can be neutral (Cao et al., 2022).

3 Theory of gas scrubbing

A reduction of acid gasses can be achieved by caustic scrubbing in a packed bed column but before experimentation, it is important to study the mass transfer theory to understand how the interaction between gas and solvent is performed.

3.1 Thermodynamics of phase equilibria

The equilibrium will describe how the chemical species of a component are distributed between the vapor and the liquid phase in a closed vessel until there mass transfer is equal on both phases. The concentration of the vapor phase is known as the vapor pressure of the compound and the concentration at each phase will depend on temperature and initial concentration of the compound. Vapor pressure refers to the inclination of a liquid to transform into vapor at a particular temperature. Greater vapor pressures indicate that more force is required to confine the molecules in the liquid phase. Conversely, lower pressures encourage the molecules to shift into the vapor phase.

The vapor pressure value can indicate how easy is it for the compound to evaporate or for its particles to escape from the liquid phase. If a compound has low vapor pressure at normal temperature then its considered to be at a solid state, and if it has high vapor pressure at normal temperature conditions is considered as a volatile material. A fast way to calculate the vapor pressure is by using Antoine's equation. The concentrations in the vapor-liquid equilibrium can be calculated by experimental data or models like Raoult, Dalton or Henrys law. The concentration of the gas in the gas phase and in the liquid phase after equilibrium gives enough values to build an equilibrium curve. The curves will be different if other solvents and other gasses are used.

In a mixture of gasses, each gas will have a pressure that is equal to the vapor pressure if it is alone in the original volume of the mixture at the same temperature conditions. The partial pressure of each gas in an ideal mixture is equal to the vapor pressure of the pure component multiplied by its mol fraction in the mixture. This law is valid for dilute phases and low pressure systems. In order for this equation to work the conditions must be ideal; so, no liquid-liquid or gas-gas interaction must take place.

$$P_{solution} = P_{solvent}^o x_{solvent} \quad (1)$$

$$P_T = P_A^* x_A + P_B^* x_B \quad (2)$$

Where $P_{solution}$ is the pressure of the solution, $P_{solvent}^o$ is the partial pressure of the pure gas and $x_{solvent}$ is the mol fraction of the gas in the mixture.

P_T is total pressure for a binary system composing of A and B, resulting from the sum of the partial pressures. When Raoult's law is not used due to non-ideal behaviour the model will deviate leading to azeotropic formations and positive or negative deviations.

3.2 Mass transfer

The final concentration of the gas dissolved into the liquid is the gas solubility in the liquid at specific temperature and pressure conditions. In a gas-liquid interaction where a non-volatile liquid and a gas mixture enter in contact, some of the components present in the gas will dissolve in the liquid fraction. The concentration of the dissolved gas in the liquid will be given by the gas solubility value at determined pressure and temperature. As an example, if there is ammonia and water in a vessel, some particles will travel from the gas phase to the liquid phase and ammonia will be present in both phases. If more ammonia is added then more ammonia will dissolve in water and a new equilibrium will be reached, where the liquid phase and the gas phase will have higher ammonia concentrations. This equilibrium between both concentrations is known as the equilibrium distribution curve or solubility curve.

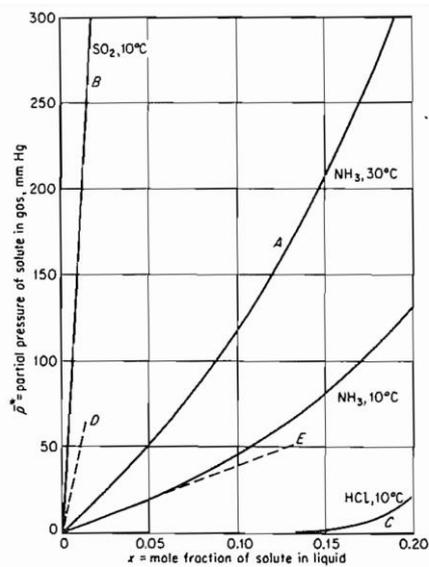


Figure 3. Gas solubility on water (Treybal, 1980).

As seen in Figure 3, if we compare ammonia (NH_3), chlorohydric acid (HCl) and sulphur dioxide (SO_2) we will see that at 10°C the solubility of HCl in water is better than SO_2 under the same conditions. Also, if we increase the temperature from 10 to 30°C in an ammonia-water interaction, the solubility of ammonia decreases. Usually when the temperature is increasing the solubility of the gas decreases. The operating conditions will depend on the gas that is being used but high soluble gases have low partial pressures since they tend to stay in the liquid phase very easily. When there is a gas mixture and they do not follow an ideal behaviour (dilute solution) then Raoult's law cannot be used anymore, so Henry's law real gas models is used. If the pressure increases in the system, then the partial pressures of the gasses increase and so on the gas solubility increase. It predicts a linear equilibrium relationship which is mainly achieved in the low concentration parts where the non-ideal solution curve and the Henry's line share the linear relationship.

$$P^* = H(x_i) \quad (3)$$

Where P^* is the partial pressure, H the Henry constant and x_i the mol fraction of the gas.

- H is the Henry's constant, and it will depend on the temperature.
- x_i is the value of gas molecules that are present in the liquid phase.

The line obtained with the Henry's values can only be related to the non-ideal solution curve when the concentrations are low, meaning only under dilute conditions. If the temperature

decreases, then Henry's constant increase and the solubility increases since the slope of the Henry's line get bigger.

3.2.1 Molecular diffusion

Diffusion is the movement of particles due to thermal conditions where the rate of diffusion can be calculated by dividing the total distance that the gas travelled during diffusion over the amount of time. If the temperature increases, then the diffusion of particles will be faster because the distance increase and time decrease. If the pressure is increased, then the diffusion moves slower and so on the time of the diffusion increase. The molecules tend to travel mostly in straight lines, but the collisions alter their path and start something called as random-walk process. Turbulent motion changes the transfer conditions from diffusion to convection, achieving higher mass transfer rates. Diffusion will predominate only in stagnant fluids or in laminar flows, traveling from the high concentration phase to the low concentration phase. In a non-uniform solution that contains two constituents, both will have to diffuse leading to have a flux J , which is the flux relative to the average molar velocity of all the constituents and describe the motion as seen in Eq. (4). J is related to the nature of the constituents.

Fick law considers the diffusion in an isobaric and isothermal binary system of two gas components, a random gas A and a random gas B . The molar flux of the specie A (J_A) and B (J_B) is proportional to the variation in concentration per the distance travelled as seen in Eq. (4) and (5). The flow goes from the specie with high concentration to the one with low concentration.

$$J_A = -D_{AB} \frac{dc_A}{dz} \quad (4)$$

$$J_B = -D_{BA} \frac{dc_B}{dz} \quad (5)$$

D_{AB} is the diffusion coefficient of gas A traveling to gas B and $\frac{dc_A}{dz}$ is the variation in concentration of gas A over the variation in distance z . In equimolar counter diffusion we have the same amount of moles going from gas A to gas B and vice versa. The molar flux of A and B are equal but in different direction $J_A = -J_B$.

$$J_A = -\frac{D_{AB}(P_{A2}-P_{A1})}{RT(z_2-z_1)} \quad (6)$$

$$J_B = -\frac{D_{AB}(P_{B1}-P_{B2})}{RT(z_2-z_1)} \quad (7)$$

For Eq. (6) and (7), R is the universal gas constant, T is the temperature and $P_{A2} - P_{A1}$ is the difference in pressures of gas A from point 2 to 1. In gases it is better to work with partial pressure than concentrations. If the diffusion is unimolecular then one component will diffuse into another that is stagnant. For example, we can take benzene diffusion into a stagnant or non-diffusing component which can be air, this case of diffusion is called Stefan flow. Other example can be ammonia into water, where water is not diffusing but ammonia diffuses into water. This kind of operation is used for absorption processes.

3.2.2 Convection

In turbulent flows it is impossible to model mathematic equations to describe what will happen, so we rely mostly in experimental data. Penetration theory contemplates a bubble of gas that raise through a liquid absorbing the gas. A particle of the liquid in a specific position around the bubble will have a finite amount of contact time, until the particle of the liquid goes around the diameter of the bubble and then leave it. If there are eddies, then the contact time will be higher, and the time of exposure will be taken as constant for all the eddies. The concentration of the gas dissolved in the eddies is considered as constant and it can be estimated by determining the variation of the concentration over the contact time.

As an example, if benzene is kept at 6 °C then the vapor will start to diffuse slowly into air and we can use Fick law for the calculations but if benzene is heated up to 80 °C then the interaction between the two phases is not controlled by diffusion but by an increase in vapor levels creating turbulence and the diffusion turns into convection. In engineering usually there must be a stage is favoured, where it could be laminar or turbulent flow to work with diffusion or convection but cases where there is diffusion and convection are avoided due to the complexity of the modelling. In convection the approach is based on mass transfer coefficient k on Eq. (10). Convective mass transfer occurs due to bulk motion, so we need to consider the velocity of the fluid. Convection is forced by adding energy (forced convection) or free where it happens alone. In order to calculate the molar fluxes, we need to calculate mass transfer coefficients k .

$$N_A = -k \Delta C \quad (10)$$

Where N_A is the flux of a gas A relative to a fixed location; k is the mass transfer coefficient; and ΔC is the variation in concentration. The two-film theory where the gas and liquid are in contact is very important to determine how the mass transfer will occur. This is the basis knowledge for gas absorption.

3.2.3 Film theory and solubility curve

As an example we will have a scrubbing system where a mixture of gases comprised by ammonia and air contacting a liquid solvent. Here the ammonia concentrations will be divided into the ammonia present in air and the ammonia present in the liquid. With the concentration values over time, we can build a solubility curve that will show what is the concentration in both phases at a certain time. If the ammonia content in the air mixture increases then the equilibrium will force the ammonia to go more to the liquid solution as well, this can be seen as a constant redistribution of solvent in both the gas and the liquid phase. Both phases must be in direct contact in order to achieve equilibrium conditions so x_i and y_i are related via the equilibrium curve. Each solubility curve is achieved at constant temperature and pressure, so if pressure increases then the solubility and the concentration of the gas in the water will increase and at lower pressure the gas will leave the liquid solution increasing the concentration in the gas phase. In absorption processes we will make a curve that predicts the solubility of the gases, meanwhile in distillation we will have the volatilities of the components where the curve will show the equilibrium relation between two volatile components, for example water and methanol. For gas absorption is a different case whereas stated before we will have a gas like ammonia distributed in the gas and liquid phase, so minimum three components are needed, and we need to know how the solubility behaves at certain constant temperature and pressure. With this at any point we choose in the curve it will be the solubility of the gas at that specific temperature.

The gas absorption operation involves the mass transfer from gas to liquid phase. We will see how the gas molecules diffuse from the bulk gas phase to the interphase with the liquid. Once the molecules arrive to this interphase, they will start to cross the border to the liquid phase and start diffusing in the liquid body. There are three flow regimes starting with the furthest point from the interphase. At the furthest point the turbulence is fully developed and

most of the mass transfer process is driven by eddy diffusion, since there is where the gas flow is more powerful. As the gas approaches to the interphase we will see that it changes to the transition zone where the flow behaves more in a laminar way but still with some turbulence. At the last phase, which is the closest to the interphase is where the gas flow behaves as a laminar flow and there is molecular diffusion. The one film theory is difficult to design since the different turbulent and laminar flows variate, so to have a simplified and useful basis for engineering analysis we will use a two-film theory. This theory will allow us to use correlations for the mass transfer phenomena since we can measure parameter like viscosity of the air, temperature, density or velocity, the things that are difficult to measure are the eddies dimensions, velocity, the width of the turbulent region and the transition zone.

For the two-film theory we have one film of gas and the other film of liquid, and we will consider an interphase between the two phases. There will be one interaction area in the gas phase and other in the liquid phase where each will have a concentration of the dissolved gas A , y_{Ai} and x_{Ai} as shown in Figure 4.

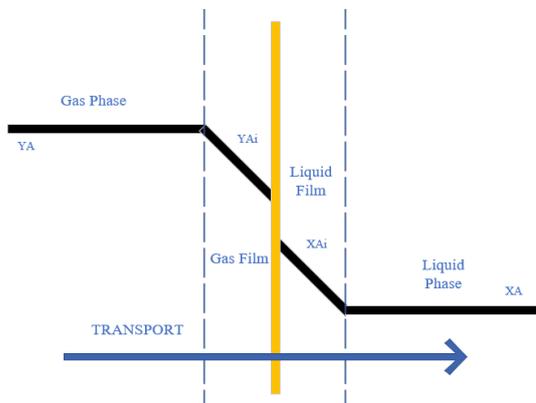


Figure 4. Two film theory in gas-liquid mass transfer operation

The reference point can be taken at any point in the column since the gas and liquid streams are flowing in opposite directions. The analysis will be performed mostly in the bulk gas phase and in the bulk liquid phase, as the bulk gas approaches the gas film the concentration drops until it reaches the interphase. The analysis is based on analysing how the diffusion of the solute A goes from the gas phase into the liquid phase. The assumptions considered to use this kind of system is that it must be in steady state where the concentration, velocities, densities and the rest of parameters do not change with time. We will have a sharp and clear boundary between the liquid and the gas, which is not real because usually the gas and liquid contact is achieved through bubbles. We assume laminar flow meaning that the bulk of both

phases is at turbulent flow and the gas and liquid film are in laminar flow. There is equilibrium between both phases where the liquid phase and the gas phase are in constant diffusion, so pressure and concentration are in equilibrium. If there are reactions between the phases, then we cannot use the two-film theory anymore.

To build the graph we need to have the concentrations at the bulk and at the interface, with the concentrations at the interphase we will have the equilibrium curve and the concentrations in the bulk phase give us the point P which is the bulk conditions or operation point for this case. M is the point of equilibrium between the gas and the liquid phase. Point E is the intersection between the concentration in the bulk liquid (x_{AL}) and the concentration of the gas phase after the interphase (y_{A^*}). Point D is the opposite of point E , having now the concentration of the gas bulk phase. The slope values are important for calculating the mass transfer coefficients.

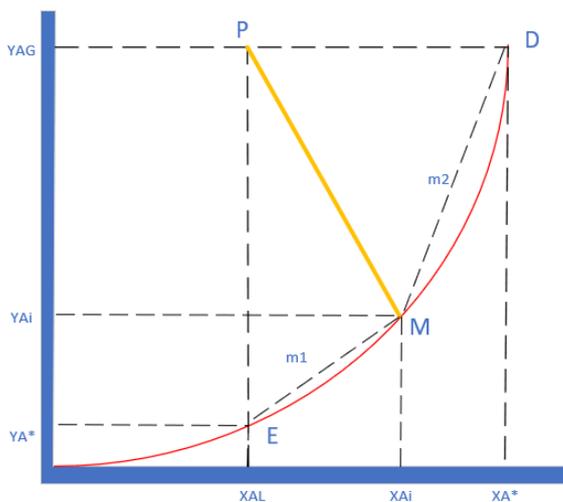


Figure 5. Equilibrium curve and operation line for a gas-liquid mass transfer system

The line from the bulk concentrations to the interphase concentrations from P to M is known as the driving force, the further the points are located the stronger will be the driving force. The driving force measures how fast will be the mass transfer achieved.

In the commercial absorption equipment, the liquid and gas phases are usually in turbulent flow and so on the film thickness will not be easy to determine, making not convenient to use Fick's law for this purpose. Instead, we can use a mass transfer equation which states that the molar flow is equal to a mass transfer coefficient multiplied by the driving force.

Including the mass transfer coefficient k leads to the overall mass transfer term:

$$N_A = k_x(x_{Ai} - x_{AL}) \quad (11)$$

In Eq. (11) and (12), N_A is the molar flux, k_x the mass transfer coefficient of the liquid phase and inside the parenthesis we have the concentration driving force in the liquid phase, being x_{Ai} and y_{Ai} the molar fraction of the liquid and gas at the interphase and x_{AL} and y_{AG} the molar fraction of the liquid and gas at the bulk. The hard part of the equation is to find the mass transfer coefficients since the concentrations of the bulk and the interphase can be found using Henry's law, because it is the driving force. The k values are determined usually experimentally or by using correlations. The driving force line drawn from the bulk conditions to the equilibrium at the interphase has a slope which is equal to the mass transfer coefficient in the liquid phase k_x over the mass transfer coefficient in the gas phase k_y .

$$\frac{(y_{AG}-y_{Ai})}{(x_{AL}-x_{Ai})} = -\frac{k_x}{k_y} \quad (12)$$

By this equation we can see that even if we don't have the values at the interphase, if we know the concentrations at the bulk and the mass transfer coefficients then we can calculate the concentration conditions at the interphase using the equation.

In the interphase it is difficult to measure the concentrations, so to avoid this we can use the overall mass transfer coefficients. For this we will need the equilibrium conditions for both bulk concentrations. The new values obtained will be x^* and y^* , so the equation now will be:

$$N_A = K_x(x_{A^*} - x_{AL}) \quad (13)$$

$$N_A = K_y(y_{AG} - y_{A^*}) \quad (14)$$

where K is the overall mass transfer coefficient, x^* the concentration of liquid at equilibrium in the bulk and y^* the concentration of gas at equilibrium in the bulk. All done to reduce the workload and complexity in measuring interphase concentrations. These will also give place to two new points that have different slopes and are located along the equilibrium line. The local mass transfer coefficients are related with the mol fraction in the vapor and liquid phase at the interphase and the overall mass transfer is related with the equilibrium at the bulk conditions. If the aim is to increase N_A , then we can increase the value of the mass transfer coefficients.

3.3 Gas absorption

Gas absorption, also known as scrubbing, involves bringing a specific gas mixture into contact with a liquid with the aim of dissolving one or more of the gas components into the liquid solvent.

The solute is the compound in the gas stream that we want to remove and that will react with the liquid phase. When water or oil are being used as the absorbents then there is no chemical reaction produced between the absorbent and the solute, turning the process into physical absorption. The liquid used for the absorption must be non-volatile, so no extra gases go to the outlet gas phase. Typical operations in the chemical industry are performed under isobaric and isothermal conditions but, to maximize the absorption, pressures should be high and temperatures low in the column. This reduces the number of stages required to achieve the desired outlet gas composition, decrease the solvent flow rate and solvent amount, and reduces the volume of the main equipment. Compression and refrigeration are expensive to maintain in an industrial process so usually the column is operated at the same pressure of the feed gas which can sometimes be higher than ambient pressure. Absorption can be driven in tray or plate, or stage columns where in each tray gas and liquid interact with each other, packed columns where the interaction is performed according to the package used in the column, spray towers and bubble columns. For the absorber, the pressure must be high and the temperature low. The objective in the absorber is to increase or maximize the number of bubbles produced so they can have a better interaction with the liquid solvent. For this study, the attention will be focused mostly on counter current operation in packed bed columns and their design.

3.3.1 Spray columns

The gas is continuously flowing upward through an open chamber where liquid droplets fall from spray nozzles to get in contact with the gas. The lower the size of the droplet the higher will be the interaction with the gas particles due to a high surface area of contact. This kind of column is widely used because it is very simple to scale, have a low pressure drop and high resistance to scale deposition and plugging

3.3.2 Bubble columns

In the bubble columns the gas is pressurized and released through a perforated pipe submerged in the scrubbing liquid, meaning that the gas phase is the one dispersed and the liquid solution is maintained continuous. As the bubbles rise in the column the absorption of the gas occurs. This kind of equipment suffer from high pressure drops due to the height of the tower and the amount of solvent present in it.

3.3.3 Tray columns

Trays are designed to act as equilibrium stages where the liquid gas interaction favours gas absorption. A typical absorption unit has from one to twenty stages. Every tray is comprised by three sections which are, the metal weir that controls the amount of solvent in the tray, the bubbling area that considers all the holes in the tray and the down comer that allows the solvent to go between stages. Trays designs are divided in sieve, valve and bubble cap, each with different advantages and disadvantages that will depend directly on the solvent and gas components used for the absorption. Usually, tray columns are used when there are low liquid rates, large number of stages or diameters, high residence times and dirty cleaning procedures. Counter current columns are widely used in industry due to their convenience for mass transfer, the gas concentration of the solute decrease as it goes up the column and the solvent gas concentration will increase. At the moment of designing the column the notation must be in the same units putting the correct numbers and letters for the gas and liquid flows and mol fractions. The operation line shows the working conditions of the operation and then is compared with the equilibrium curve for the system. The operation line shows the relationship between the gas flux, liquid solvent flux and the molar fraction of each. The equation to obtain the line is obtained by performing a simple material balance around the column where mass in=mass out.

3.3.4 Packed columns

The typical conditions required is that the gas must be soluble in the solvent, the solvent must not be volatile at operation pressure and temperature conditions, it cannot be corrosive,

the cost must be low, viscosity low and must be safe to use for the environment or people. High viscosity will cause low liquid flow, flooding, and high pressure drops. Chemical reactions will result in high gas solubility. Packed bed materials will cause the gas to go through a longer path or tortuosity increasing the interaction between gas and liquid. It is particularly important to consider the height and diameter of the column since there will be higher pressure loss due to the packed bed material. To design a packed column, we will need the equilibrium data of the gas-liquid system to know the mass transfer and to locate the points of the operation line and equilibrium curve. We need to know the liquid and gas flow rates, the solute concentration at two different points so we can build the operation line and finally the individual and overall mass transfer coefficients to design packed absorption towers. The steps to design a packed bed column can be followed as:

1. Select the solvent that must not be viscous or volatile.
2. Selection of the packing material that will go in the column.
3. Calculate the minimum solvent flow rate and the actual solvent flow rate..
4. The column diameter, based on the drop in pressure expected for the selected package.
5. Height of the column, based on the diameter, based on the amount of packing.
6. Design of solvent distributors and redistributors.
7. Design of the gas distributor, packing support, shell, nozzles, column support, all technical things that form part of the column.

Packed columns tend to be more expensive than tray columns, but the packaging materials favour the interaction between gas and liquid. The best conditions for packed columns are with small diameters with less than 0.6 m where lower pressure drop is achieved, and foaming can be handled easier.

The packing is anything that goes in the column that help the gas-liquid interaction, and it must not corrode during the process or release unwanted chemicals into the process. The package material can be dumped at random order in the column favouring randomness and longer pathways or it can be structured package or grid packings. The package must be strong to resist the absorption process, low in weight, with exact void volume in the packing

passages to let enough gas and liquid to interact, wide surface area, low cost, always available, easy to replace and resistant to fouling so solids cannot stick to their surface. Metals are usually preferred due to their strength and capability to hold a good liquid layer around them so there is better gas-liquid interaction, this is called as wettability. Plastics are inexpensive materials which have a high strength but poor wettability at low liquid rates. Ceramics are useful when working with elevated temperatures and corrosion with good wettability, but they do not have a good mechanical strength. Random packings are the most popular way to arrange a column in industrial applications, packages are dumped into the column during the installation falling randomly. Stacked packing can favour the decrease in pressure but it decreases the path length flow in case that time residence is an issue. Structured packaging is more expensive to design and build but they will give less pressure drop with high efficiency and high capacity of liquid and gas flow rates.

4 Materials and methods

4.1 Process description and mechanism

The experimental part of this thesis consists in three different analyses with different goals to achieve. The first experiment was to determine how the concentration of sodium hydroxide affects CO₂ absorption by using a simulated gas mixture, composing of carbon dioxide and nitrogen. The second experiment, performed using a fixed concentration of 25.65 g/L of NaOH while varying the amount of glass bottles. The goal is to resemble the stages of a tray column and analyse the carbon dioxide concentration obtained at the outlet. The third experiment consist in using the best absorption system from the second experiment and analyse if methane is absorbed by the solvent. The CO₂ concentrations were measured using an ABB AO2020 (ABB, Finland) for concentrations above 200 ppm and a Jetanizer GC equipment (activated research company, USA) for lower concentrations than 200 ppm.

4.2 Experimental methodologies

4.2.1 Effect of caustic solvent concentration

In this experiment three different concentrations of caustic solution were employed to determine the effect of CO₂ removal from the main gas stream. The first experiments consisted in a small-scale caustic scrubbing procedure where glass bottles functioned as column stages. The pH values for the alkaline aqueous solutions at different NaOH concentrations are given in Table 4.

Table 4. Concentration and pH values for the three alkaline solutions used for the experiment.

Concentration		pH
NaOH		
0.1276	g/L	11
1.2795	g/L	13
12.774	g/L	14

The experimental setup consisted in different mass flow controllers for gas feed, glass bottles that simulate the stages of a tray column, flow and pressure meters, temperature meters and an ABB AO2020 gas analyser. Figure 6 illustrate the setup of the experiment. The bottles are aligned in a series combination while using glassware tubing and metal handles to prevent gas leakage. The two initial glass bottles contain the caustic solvent while the third contains distillate water constantly cooled down using a vessel to act as a water condenser, see Figure 6.

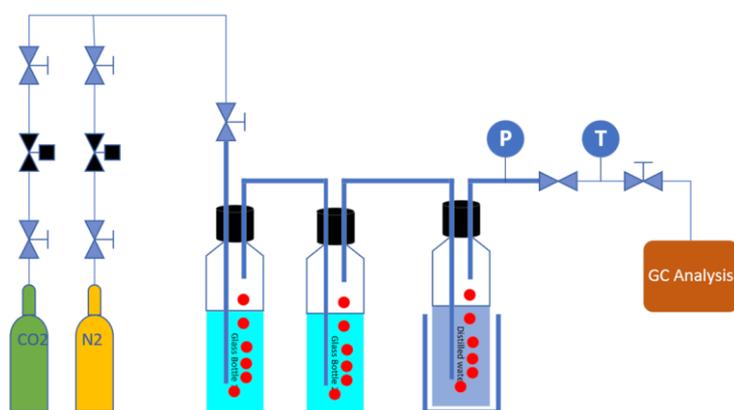


Figure 6. Simplified scheme of the set up used for the first experiment.

The simulated pyrolysis gas consists of a mixture of 99 vol% N_2 and 1 vol% CO_2 . Once the values are set, then the manual valves of CO_2 and N_2 are opened, leaving only the electric valves closed. At the beginning of the experiment only the N_2 electric valve is opened to allow the nitrogen flow through the piping system and remove other gases and impurities that might be present from previous experiments. When the measured gas at the outlet shows only nitrogen coming out, then the flux going to the glass bottles is disrupted and redirected to a flow measurement equipment using a bypass. When the bypass is closed, the carbon dioxide electric valve was opened, allowing both gases to mix and reach their original flow of $1 \text{ dm}^3/\text{min}$. After measuring the gas flow, temperature and pressure, the system was ready for the absorption process.

When the outlet CO_2 concentration show a constant behaviour, the bypass is opened to allow the CO_2 flow through the bottles and contact the caustic solution. High volume flow, wide inlet glass pipe diameter and turbulence of the gas at the inlet allowed to form medium sized bubbles with a large surface area. With medium sized bubbles the mass transfer is not efficient, but since it is a continuous system of bottles the gas that did not reacted in the first bottle will react in the second and so on with the rest. The reaction between CO_2 and $NaOH$ is exothermic, causing an increase in the temperature of the solvent and so on generating small amounts of water vapor that are carried along with the outlet gas. To prevent water vapor going to the gas measuring equipment, a wide glass bottle submerged in ice was implanted after the last glass bottle stage to function as a condenser. This to prevent water vapor reaching the gas analysis equipment since it causes damage and corrosion.

Pressure (P) and temperature (T) levels are kept constant during all the process and measured at the outlet of the system. There were small increments in temperature due to the exothermic

reactions taking place. The first experiments were performed using the fixed parameters presented in Table 5, which were maintained through the experiments using only the water-sodium hydroxide solution as solvent.

Table 5. Fixed operating parameters used for the CO₂ absorption experiments at different alkaline solvent concentrations.

Parameter	Value	Units
Gas volume flow	1.022	dm ³ /min
Volume per bottle	200	mL
Number of bottles	2	
Caustic component used	NaOH	
Temperature of gases	28.07	°C
Pressure difference	0.07	bar

Table 6. Composition and flow of the gas feed entering the process.

	Volume fraction [vol%]	Volume flow [dm ³ /min]
Nitrogen	99%	0.99
Carbon dioxide	1%	0.01

The first experiments included six test runs where the experiment with each concentration was repeated twice. The samples containing CO₂ are measured every minute using a gas chromatograph ABB AO2020.

4.2.2 Effect of number of stages (vials)

A higher concentration improves the efficiency of CO₂ removal. Now for this experiment the purpose was to keep the caustic concentration at a constant high value of 25.65 g/L NaOH and variate the reaction time of gas with the solvent using different number of bottles. The setup was similar to the one used in the previous experiment, with the difference that instead of a glass bottle with distillate water submerged in ice, now there was one bottle without any content inside, see Figure 7. This adaptation was performed since the ppm levels at the outlet

are getting lower every time and the carbon dioxide present in the distillate water condenser may affect the outlet CO₂ levels.

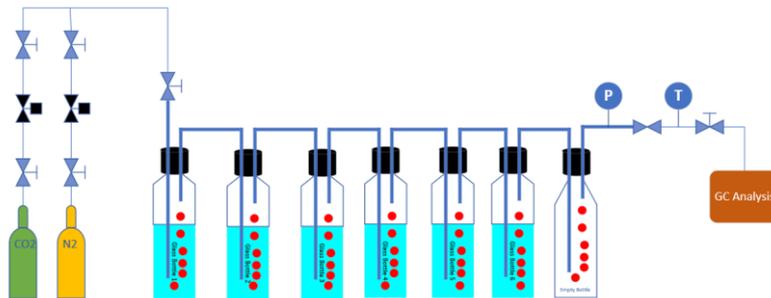


Figure 7. Simplified diagram of scheme of CO₂ capture from a CO₂/N₂ gas feed by using a constant NaOH solvent concentration at room temperature and pressure.

Temperature and pressure obtained by the system sensors were useful to calculate the inlet gas flow (1 dm³/min with 99 vol% N₂ and 1 vol% CO₂). The volume present in each glass vessel was at 150 mL to prevent overflow and a pump was used to prevent high pressure drops and ensuring a constant gas flow through each bottle. The reduction of pressure drop improve the bubble gas-solvent contact through all the system since the gas flow is strong in all the stages. The gas composition obtained from the one bottle and two bottle system were analysed using the ABB AO2020 equipment for volume percent concentrations and then for the three, four, five and six bottle system a GC Jetanizer analyser was used to for ppm concentrations.

Table 7. Initial conditions of gas flow, concentration, temperature and pressure of the six experiments, inlet CO₂ flow of 0.01 dm³/min.

	Number of bottles	Bottle solvent volume [mL]	Temperature [°C]	Pressure [bar(g)]	Duration of experiment [min]
ABB AO2020	1	200	19	0.01	47
ABB AO2020	2	200	19	0.01	38
GC Jetanizer	3	150	20	0.08	100
GC Jetanizer	4	150	20	0.08	93
GC Jetanizer	5	150	19	0.07	100
GC Jetanizer	6	150	19	0.05	100

As seen in Table 7 the duration of the experiments after the two bottle experiments increased, this due to the 15 minutes it takes for the GC Jetanizer to analyse each sample of the gas. The results could keep going for more hours, but the main goal in these experiments is to determine what is the lowest concentration that can be achieved at the beginning of the reaction. At the end of the experiment, we retrieved the carbon dioxide outlet concentrations from the GC software and analysed them with respect to time.

4.2.3 Effect of methane on carbon capture using an alkaline solvent

After demonstrating that caustic solution at high concentrations can remove vast amounts of carbon dioxide down to 6 ppm, it is important to test other gasses that might get absorbed like organic compounds. For this test the organic compound selected was methane and it was injected with the feed gas comprised of the volume fraction presented in Table 8.

Table 8. Flow rate and composition of CO₂/N₂/CH₄ mixture for carbon capture tests.

	Volume fraction [vol%]	Volume flow [dm ³ /min]
Nitrogen	69%	0.69
Carbon dioxide	1%	0.01
Methane	30%	0.30

The initial operating conditions used for this experiment were the same as the 6-bottle system presented in Table 7.

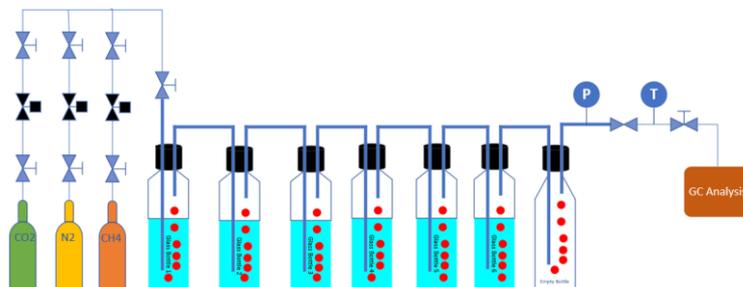


Figure 8. Simplified diagram of a 6-bottle scheme for CO₂ capture from a CO₂/N₂/CH₄ gas feed by using a constant NaOH solvent concentration at room temperature and pressure.

5 Results and Discussions

5.1 Effect of alkaline solution concentration

The aim of the experiments performed in this section was to test how different caustic solvent concentrations affect the CO₂ levels of a CO₂/N₂ inlet gas. The results showed that as NaOH concentrations increase, the removal of carbon dioxide from the feed gas stream improves. The changes in pH and concentration of the caustic solution are related to the velocity and absorption degree of the gas in the solution. At pH values below 8 the reaction starts with the CO₂ reacting with water to produce carbonic acid which later reacts with NaOH to produce sodium bicarbonate. This due to the low concentration of NaOH, meaning less molecules of NaOH will react with CO₂. At a pH above 10 the reaction takes a different path because there is excess of NaOH present in the solution, leading to the following reactions:



The products formed are governed by the concentration of the reactants and the operating conditions that for this case are at room temperature and pressure. Reaction Eq. (15) is the first to take place since CO₂ is an acid gas and NaOH a strong base, leading to achieve high reaction rates, while producing sodium bicarbonate (*NaHCO₃*). The reaction rate is the variation of the concentration over the change in time, where the rate for the reactants is negative since it represents a reduction in the concentration. The enhancement factor is the ratio between the absorption in under the effect of a chemical reaction, over the physical absorption. The enhancement factor using caustic solvents is high due chemical reaction have a higher enhancement factor if compared to physical CO₂ absorption. Figure 9 represent the graph obtained after the reaction of an inlet gas flow comprised of 1 vol% CO₂ and 99 vol% N₂ with a caustic solvent 1.2795 g NaOH. The values plotted in the graph are the outlet concentrations of CO₂ in function of the reaction time. The graph is comprised of two regions, a yellow region represented with the letter M which represents the variation in the concentration of CO₂ for the first 3 hours of reaction, and a region N Which represent the variation in the concentration of CO₂ after 3 hours of reaction. The slope of the graph of

region M is obtained from reaction Eq. (15), where a pronounced inclination can be appreciated, meaning it has a high reaction rate and so on it is the fastest reaction between Eq. (15) and (16).

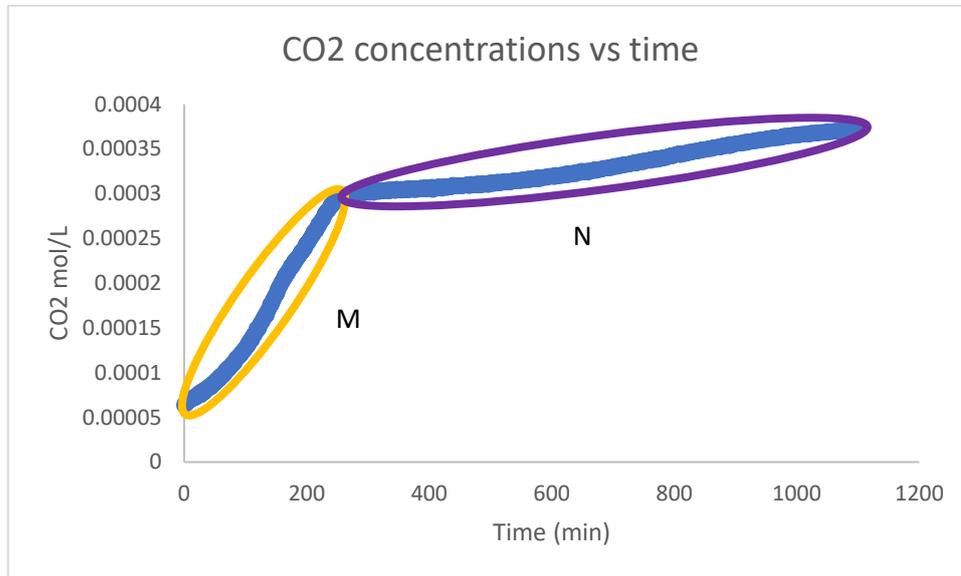


Figure 9. CO₂ concentration at the outlet using a caustic concentration of 1.2795 g/L NaOH. Gas flow 1 dm³/min, and concentration 1% CO₂, 99% N₂. M and N are two reactions regimes related to Eq. (15) and (16).

The mass transfer enhancement is high when the pH levels are high, meaning that the effect of the chemical reactions taking place will cause most of the absorption. As the reaction advances, more sodium bicarbonate is produced, leading to Eq. (16) where the sodium bicarbonate start to react with the remaining NaOH. As shown in Figure 9, the region N represented by the purple line is the variation of concentration of CO₂ with respect to time. In this part we can appreciate that the concentration of CO₂ slowly increases trough time, showing that small amounts of CO₂ are reacting in the solution, but the main reaction that takes place is between the sodium bicarbonate and NaOH to produce sodium carbonate. The less pronounced slope created by the graph in section N, shows that the reaction rate is low and so on we are facing a slow reaction. Once all the NaOH present in the solvent has reacted, the reaction stops and the CO₂ levels from the inlet equal the CO₂ at the outlet, meaning there is no absorption.

The three NaOH concentrations used for this experiment were increased in a ratio of 1, 10 and 100, being 12.77 g/L the highest concentration tested. The lowest value reached with the highest caustic concentration was 1700 ppm as presented in Table 9.

Table 9. The lowest CO₂ concentrations achieved at the outlet, $T=25^{\circ}\text{C}$, $P=1$ bar, gas flow 1 dm³/min, concentration 1% CO₂, 99% N₂.

Solvent concentration [g/L]	Lowest CO ₂ concentration [ppm]
0.1276	5179
1.2795	4300
12.774	1700

After analysing the outlet concentrations of CO₂ presented in Table 9, we can deduce that the higher the concentration of the caustic solution, the more CO₂ from the feed gas will react. The third caustic solvent concentration is the highest, so it has a major influence on the absorption of carbon dioxide.

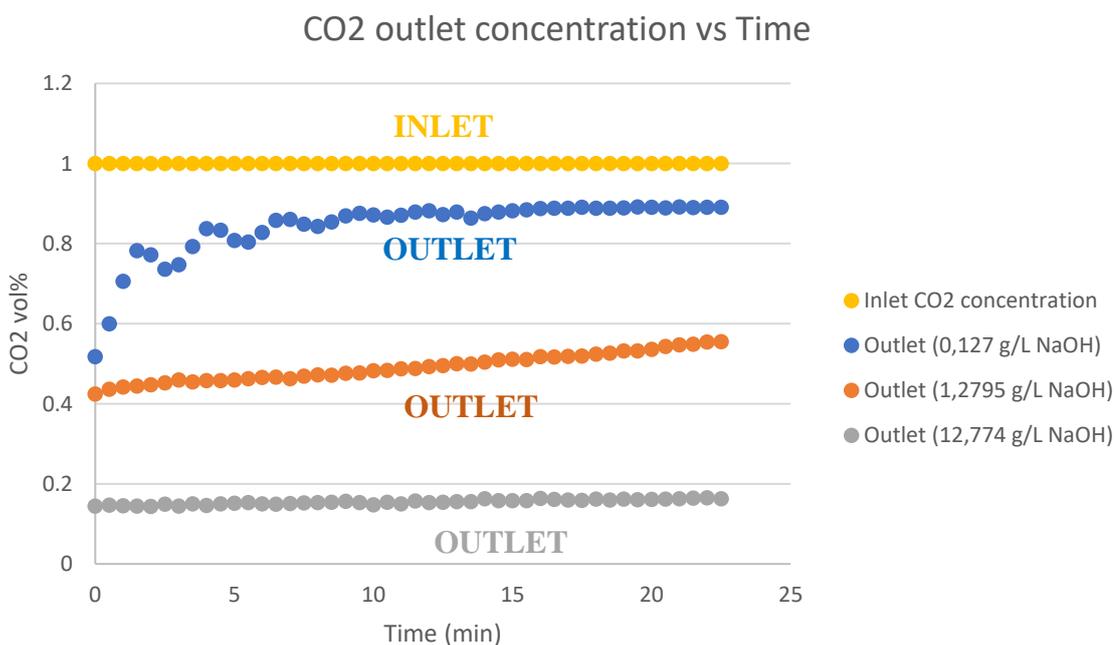


Figure 10. Volume percent of carbon dioxide achieved at the outlet while using a 2-bottle system. Gas flow of 1 dm³/min and concentration of 1% CO₂, 99% N₂.

Figure 10 is a representation of the outlet volume percentages of CO₂ in the first 20 minutes of reaction. Each colour represents a specific caustic concentration, and the three experiments are compared with the CO₂ concentration at the inlet. As shown in Figure 10, CO₂ reacts very fast with the 0.127 g/L NaOH, where 10 minutes after the reaction started,

most of the NaOH is consumed. For the concentrations of 1.27 and 12.77 g/L of NaOH, the CO₂ levels are lower and the CO₂ reacting with NaOH will take longer times until all the alkaline solvent gets consumed.

5.2 Effect of gas residence time in alkaline solution

After determining that at higher caustic solvent concentrations the removal of CO₂ increases, then the next experiments are focused on using a fixed concentration of 25.65 g/L NaOH and vary the reaction time between the gas and the solvent. Every bottle added to the system will increase the residence time of the gas in contact with the caustic solution, favouring the mass transfer and reactions in Eq. (15) and (16). Experiments were performed under different bottle volume and bottle number as presented in Table 10.

Table 10. Effect on the efficiency of CO₂ obtained at the outlet by varying the residence time between CO₂ and the caustic solution. Fixed operation conditions of 25.65 g/L NaOH, *pH* 14, 1 dm³/min gas flow 1% CO₂ 99% N₂, 28°C and *P*=1 atm.

Bottle number	1	2	3	4	5	6
Volume of caustic per bottle [mL]	200	200	150	150	150	150
Lowest CO ₂ concentration achieved [ppm]	3767.84	230.24	604.51	87.47	15.99	2.085
Residence time [seconds]	0.29	0.57	0.36	0.48	0.6	0.72

The volume poured in each bottle was about 200 mL for the first two-bottle systems, but from the third to the sixth-bottle system the volume was decreased to 150 mL. The volume reduction was due to the pressure drop caused by the 200 mL, because it was too high to support a third bottle and keep a constant gas flow through the system. To fix the problem, a pump was added to decrease the pressure drop and the volume per bottle was decreased to 150 mL each to secure a constant gas flow.

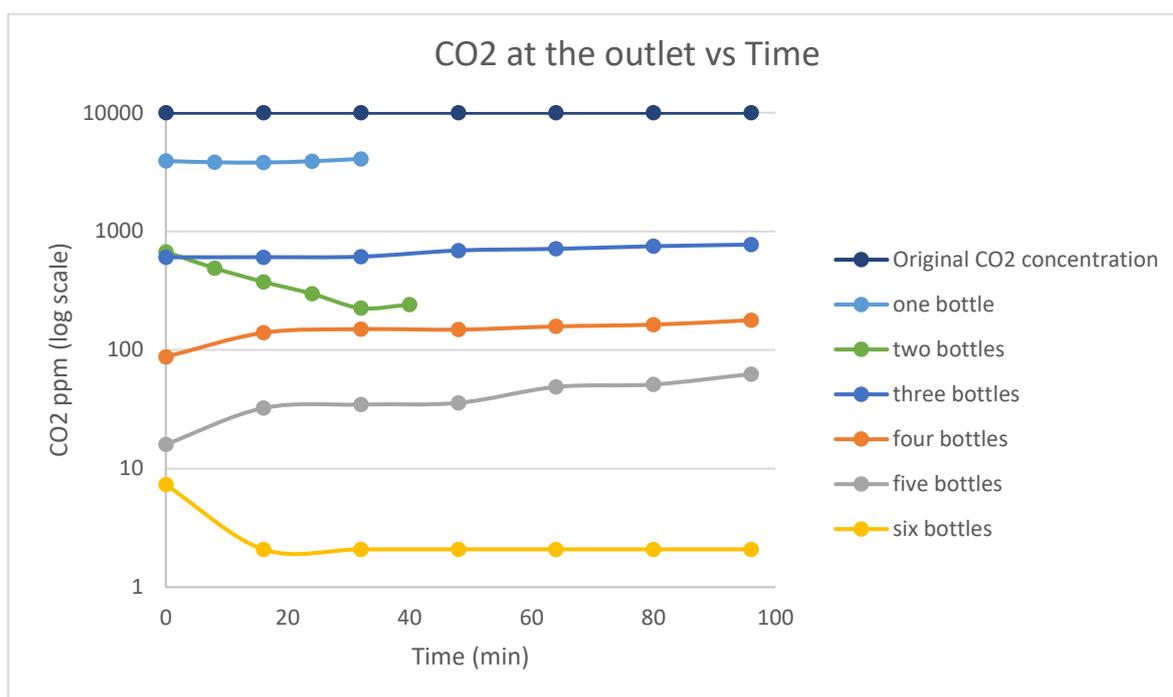


Figure 11. CO₂ concentrations at the outlet using different amounts of bottles for the system. 25.65 g/L NaOH, pH 14, 1 dm³/min gas flow 1% CO₂ 99% N₂, 28°C and 1 atm of pressure.

Figure 11 is a representation of the CO₂ ppm levels obtained at the outlet as a function of the number of bottles used in the system. The experiments that involved one and two bottles were tested for 40 minutes because the main objective was to analyse the lowest outlet concentration of CO₂ that can be achieved. The rest of experiments involving three bottles, or more were evaluated for one hour and forty minutes due to the time it took to the gas chromatograph equipment to analyse the samples.

In Figure 11 the lowest concentration achieved was 2.085 ppm with a 6-bottle system, having a total reaction time of 0.75 seconds. One reasons for having a 6-bottles and not less can be explained by the size of the gas bubbles. The bubbles had a medium size, meaning that the area of contact between the solvent and the gas was small and so on no high mass transfer were achieved. If the gas bubbles are smaller, then the mass transfer and the reaction rates increase reducing the residence times. For the system proposed in this section, longer reaction times gives a higher degree of absorption and reaction to form carbonate species. This affects the pH of the solvent due to the acidic properties of carbonic acids start to accumulate in the bottles. An excess of carbonic acid reduces the pH of the solution, leading to an increase in the precipitates production.

To understand how much caustic solution must be fed to the bottles to keep the CO₂ ppm levels under 3 ppm, we can calculate the amount of CO₂ that can be absorbed by one gram of sodium hydroxide. We use the lowest CO₂ concentration from Table 10 with the 6-bottle system and fixed concentration of 25.65 g/L NaOH used to achieve that concentration.

$$25 \frac{\text{g}}{\text{L}} \text{NaOH}(\text{solvent concentration}) * \frac{1 \text{ L}}{1000 \text{ mL}} * 900 \text{ mL} (\text{volume of 6 bottles}) = 22.5 \text{ g NaOH} (\text{total grams of NaOH in the bottles})$$

$$10000 \text{ initial CO}_2 \text{ ppm} - 2.085 \text{ final CO}_2 \text{ ppm} = 9997.92 \text{ removed CO}_2 \text{ ppm}$$

Since 9997.92 ppm of CO₂ were removed with 22.5 g of NaOH then we can analyse how many ppm are removed with one gram of NaOH.

$$\frac{9997.92 \text{ removed CO}_2 \text{ ppm}}{22.5 \text{ g NaOH}} = 444.35 \text{ ppm CO}_2$$

For every gram of NaOH present in the solution, 444.35 ppm of CO₂ will be removed in the first minute.

5.3 Effect of high alkaline concentrations on methane absorption

The acid compounds removed include carbon dioxide, hydrogen sulphide, mercaptans, phenols and organic compounds (Copa, Momont and Beula 2021). For this reason, methane, which is one of the main organic compounds present in pyrolysis gas, was introduced to the inlet of the system.

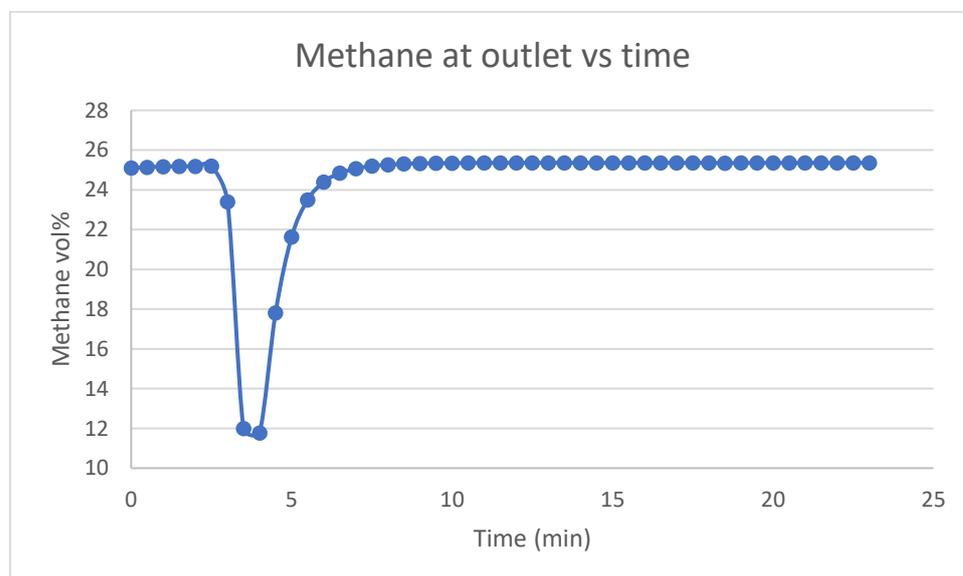


Figure 12. Volume percent of methane at the outlet under the following conditions, 25.65 g/L NaOH, $pH=14$, 1 dm³/min gas flow 1% CO₂ 99% N₂, 28°C and 1 atm of pressure.

Figure 12 shows the methane volume percentage at the outlet of the system in function of time. As shown in the graph, the decrease in concentration in the first 5 minutes of reaction is due to the nitrogen gas present in the bottles when methane started to flow into them. After the nitrogen was out of the bottle system the amounts of methane increased up to the original volume concentrations of the inlet flow, meaning that there was no reaction or interaction between the solvent and methane. As seen in Figure 12 the concentration of methane does not change when contacted with high caustic solvent concentrations.

The solubility of methane in water increases when the temperature decrease and the pressure increase. Other parameter that improve the solubility of methane in water are bubbles that can maintain a stable size of about 1.2 nm. For the experiment performed in this section, the pressure difference is very low and so on will be the solubility of methane in the solvent. At 28 °C the mole fraction of methane present in pure water is about 0.004 and for the caustic solution is 0 (Grabowska et al., 2022).

Table 11. Summary of the performed experiments with gas flow 1 L/min, 1 vol% CO₂, 99 vol% N₂

Concentrations [g/mL]	Bottle number	Bottle volume [mL]	Initial pH	Temperature [°C]	Pressure difference [bar]	Residence time per bottle [seconds]	Total experiment time [min]	Lowest CO ₂ concentration achieved [ppm]	Analysis equipment
0.1276	2	200	11	28.4	0.15	0.57	34	5179	ABB AO2020
1.2795	2	200	13	28.4	0.15	0.57	157	4300	ABB AO2020
12.774	2	200	14	28.4	0.15	0.57	360	1700	ABB AO2020
25.65	1	200	14	19	0.01	0.29	47	3767.8	ABB AO2020
25.65	2	200	14	19	0.01	0.57	38	230.24	ABB AO2020
25.65	3	150	14	20	0.08	0.36	100	604.51	GC Jetanizer

25.65	4	150	14	20	0.08	0.48	93	87.47	GC Jetanizer
25.65	5	150	14	19	0.07	0.6	100	15.99	GC Jetanizer
25.65	6	150	14	19	0.05	0.72	100	2.085	GC Jetanizer

6 Conclusions

The key parameters to test in order to achieve a higher CO₂ removal from a CO₂/N₂ feed gas are caustic concentrations and residence times. In the first experiments performed, the concentration was varied from 0.12 to 12.77 g/L NaOH. Where the best CO₂ scrubbing efficiencies were obtained with the higher concentration of NaOH while being contacted directly with a gas mixture of CO₂/N₂. Successfully, it was demonstrated that high concentrations of caustic solution improve the absorption of the acidic gas CO₂. After settling that the CO₂ removal is widely influenced by the solvent concentration, it was time to set a fixed caustic concentration of 25.65 g/L with a pH of 14 and vary the residence time between the gas and the solvent. The effect of a constant gas velocity and fixed caustic concentrations, proved to be more effective in acid gas removal efficiency while increasing the residence times. As more bottles were added to the system the residence times increased and so on the outlet concentrations of CO₂ decreased. The best system arrangement to reduce CO₂ concentrations down to 3 ppm levels was by using a 6-bottle system with a residence time of 0.72 seconds. Nevertheless, to find the best operational conditions, the gas residence time must be optimized to achieve higher CO₂ removal with shorter residence times. The operation improvement can start with further experimentation regarding temperature increase, usage of glass beads to replicate a packed bed and reduce bubble size or using magnetic stirrers to create small eddies. High alkaline concentrations can remove organic compounds present in the feed gas, so further tests after the optimization process are related to the usage of real plastics gasification syngas, performed to determine how NaOH will behave with other compounds than acid gases present in the syngas. As a starting experiment regarding organic compound removal, an additional reaction was investigated in the third experiment of this thesis to determine if the caustic concentration used for the six-bottle system was able to absorb methane. For this third experiment an inlet gas flow comprised of

$\text{CO}_2/\text{N}_2/\text{CH}_4$ was used in the six-bottle system, where after 40 minutes of reaction there was no absorption of methane in the caustic solution.

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Appendix 1. Concentrations of caustic solvents and outlet CO₂ volume percentages obtained in the alkaline solution concentration experiment

Time	CONCENTRATIONS		
	0,127 g NaOH	1,2795 g NaOH	12,774 g NaOH
0	0.517951	0.424751	0.144982
0.5	0.600362	0.436647	0.14734
1	0.706147	0.441755	0.145436
1.5	0.782629	0.444924	0.144965
2	0.772621	0.447788	0.144349
2.5	0.736563	0.452296	0.149838
3	0.747449	0.459671	0.144635
3.5	0.793212	0.454915	0.150611
4	0.837457	0.458039	0.146261
4.5	0.833805	0.458406	0.150694
5	0.807979	0.459608	0.152192
5.5	0.80425	0.463119	0.153832
6	0.828172	0.465707	0.150377
6.5	0.858206	0.466713	0.149742
7	0.860443	0.463274	0.150996
7.5	0.8491	0.469386	0.152376
8	0.842941	0.47212	0.153437
8.5	0.854279	0.471355	0.154684
9	0.869674	0.476315	0.156904
9.5	0.875571	0.47712	0.153423
10	0.871647	0.483112	0.147855
10.5	0.866621	0.483732	0.153954
11	0.870936	0.487659	0.150531
11.5	0.879058	0.488109	0.157879
12	0.882261	0.492987	0.153712
12.5	0.872305	0.495332	0.154057
13	0.878962	0.500046	0.156043
13.5	0.864222	0.49951	0.156091
14	0.875072	0.504521	0.162927
14.5	0.87868	0.510131	0.158584
15	0.88264	0.511569	0.15816
15.5	0.884752	0.511052	0.158063
16	0.887486	0.517925	0.163667
16.5	0.888574	0.516902	0.16131
17	0.888797	0.519077	0.15964
17.5	0.89138	0.519093	0.158875
18	0.888486	0.52429	0.161982
18.5	0.888709	0.52687	0.159852

19	0.889671	0.532529	0.162375
19.5	0.891639	0.532272	0.161073
20	0.890829	0.536219	0.16135
20.5	0.889662	0.543482	0.162246
21	0.891489	0.547677	0.163159
21.5	0.890001	0.549013	0.164608
22	0.890891	0.554724	0.165665
22.5	0.89092	0.55568	0.163336
23		0.557799	0.171479
23.5		0.557328	0.170344
24		0.565677	0.168421
24.5		0.571465	0.169304
25		0.57516	0.173047
25.5		0.57474	0.166794
26		0.581283	0.170451
26.5		0.583053	0.174563
27		0.584034	0.169178
27.5		0.588368	0.16928
28		0.594178	0.173257
28.5		0.593345	0.170038
29		0.599752	0.175484
29.5		0.600457	0.170103
30		0.605954	0.170802
30.5		0.60455	0.17639
31		0.61109	0.174585
31.5		0.616596	0.176455
32		0.61729	0.179439
32.5		0.622851	0.174986
33		0.620728	0.181179
33.5		0.620349	0.177906
34		0.624849	0.177898
34.5		0.629773	0.178696
35		0.631943	0.183383
35.5		0.631775	0.185032
36		0.638119	0.184107
36.5		0.637101	0.181612
37		0.639284	0.181287
37.5		0.64137	0.182237
38		0.645219	0.187275
38.5		0.644108	0.190025
39		0.650497	0.183456
39.5		0.648318	0.187085
40		0.648725	0.19225
40.5		0.648085	0.189358

41		0.65352	0.191258
41.5		0.650244	0.187894
42		0.652626	0.191679
42.5		0.654165	0.193709
43		0.657975	0.195299
43.5		0.656306	0.191186
44		0.656936	0.19446
44.5		0.652994	0.194631
45		0.657852	0.193315
45.5		0.65741	0.196263
46		0.660116	0.199278
46.5		0.65853	0.201335
47		0.6613	0.199979
47.5		0.662462	0.203394
48		0.661283	0.202046
48.5		0.675002	0.20285
49		0.667713	0.203056
49.5		0.668897	0.201712
50		0.665143	0.200198
50.5		0.664432	0.20452
51		0.665142	0.202098
51.5		0.66821	0.203759
52		0.66592	0.203594
52.5		0.665703	0.207889
53		0.664646	0.206365
53.5		0.665693	0.206592
54		0.668433	0.21053
54.5		0.665529	0.207376
55		0.668096	0.207083
55.5		0.670997	0.209806
56		0.669958	0.213399
56.5		0.671636	0.213253
57		0.668526	0.212268
57.5		0.670676	0.217637
58		0.671464	0.215662
58.5		0.67133	0.213752
59		0.670226	0.216267
59.5		0.671194	0.213804
60		0.672516	0.219214
60.5		0.671125	0.21759
61		0.673614	0.217723
61.5		0.67564	0.217928
62		0.671739	0.223753
62.5		0.674676	0.221981

63		0.675433	0.220733
63.5		0.678187	0.219152
64		0.67105	0.224753
64.5		0.677048	0.2246
65		0.677516	0.226741
65.5		0.680028	0.223442
66		0.676803	0.222239
66.5		0.68225	0.225272
67		0.680564	0.230011
67.5		0.677974	0.228042
68		0.680729	0.23139
68.5		0.685203	0.227388
69		0.690191	0.232242
69.5		0.69012	0.228336
70		0.685324	0.23604
70.5		0.686094	0.231214
71		0.68694	0.23406
71.5		0.688185	0.237144
72		0.6892	0.232752
72.5		0.691399	0.238374
73		0.693078	0.237984
73.5		0.694389	0.234758
74		0.694784	0.24276
74.5		0.696995	0.241115
75		0.695568	0.2451
75.5		0.698048	0.245142
76		0.700708	0.24521
76.5		0.699058	0.246545
77		0.704058	0.245514
77.5		0.701078	0.251666
78		0.705744	0.243596
78.5		0.707077	0.250323
79		0.711445	0.24789
79.5		0.714789	0.247931
80		0.719739	0.244219
80.5		0.72053	0.252312
81		0.723077	0.25373
81.5		0.725867	0.252449
82		0.730429	0.258496
82.5		0.728352	0.255147
83		0.732395	0.255829
83.5		0.738666	0.255496
84		0.739769	0.257517
84.5		0.743067	0.263059

85		0.7488	0.26272
85.5		0.751123	0.26333
86		0.756672	0.257362
86.5		0.762575	0.262246
87		0.764155	0.267558
87.5		0.768135	0.263101
88		0.772568	0.263424
88.5		0.775506	0.265991
89		0.777671	0.264728
89.5		0.779947	0.264599
90		0.781029	0.267826
90.5		0.784981	0.271459
91		0.784245	0.268651
91.5		0.787149	0.274341
92		0.78922	0.275401
92.5		0.791252	0.27311
93		0.792891	0.272663
93.5		0.791072	0.280799
94		0.792178	0.275215
94.5		0.793886	0.282624
95		0.792801	0.280524
95.5		0.797543	0.287738
96		0.798362	0.284765
96.5		0.79787	0.282365
97		0.800506	0.288699
97.5		0.803983	0.283513
98		0.805248	0.284373
98.5		0.805119	0.287667
99		0.808469	0.28584
99.5		0.811356	0.293381
100		0.811738	0.287905
100.5		0.81382	0.296086
101		0.819658	0.291863
101.5		0.822619	0.295724
102		0.823073	0.298105
102.5		0.8271	0.297009
103		0.828833	0.297341
103.5		0.832531	0.296319
104		0.838623	0.299205
104.5		0.842164	0.300013
105		0.845681	0.300609
105.5		0.849775	0.301382
106		0.850208	0.301841
106.5		0.854582	0.302619

107		0.85657	0.306117
107.5		0.862694	0.30812
108		0.863469	0.311595
108.5		0.867031	0.309218
109		0.866781	0.309686
109.5		0.870936	0.309336
110		0.875148	0.311022
110.5		0.875803	0.31106
111		0.876472	0.31654
111.5		0.878371	0.314839
112		0.878745	0.319129
112.5		0.880868	0.319341
113		0.881173	0.319178
113.5		0.881561	0.325188
114		0.885595	0.326608
114.5		0.884069	0.325536
115		0.887031	0.324683
115.5		0.886984	0.32817
116		0.887458	0.323445
116.5		0.888503	0.333364
117		0.890354	0.330309
117.5		0.893249	0.33087
118		0.890871	0.331695
118.5		0.890329	0.334682
119		0.890342	0.332731
119.5		0.889606	0.340777
120		0.891461	0.340801
120.5		0.890585	0.342301
121		0.890355	0.346291
121.5		0.891249	0.346507
122		0.890337	0.343605
122.5		0.8915	0.346123
123		0.892624	0.350169
123.5		0.891331	0.3517
124		0.891659	0.347411
124.5		0.892433	0.35453
125		0.895338	0.353226
125.5		0.893615	0.350937
126		0.893629	0.354158
126.5		0.893248	0.356716
127		0.893455	0.355474
127.5		0.891171	0.360422
128		0.894294	0.360058
128.5		0.894471	0.365881

129		0.8951	0.364749
129.5		0.894924	0.364974
130		0.891398	0.363318
130.5		0.89168	0.371241
131		0.892987	0.368853
131.5		0.888927	0.368535
132		0.888377	0.370075
132.5		0.888913	0.374474
133		0.888839	0.379584
133.5		0.887072	0.380609
134		0.886149	0.377503
134.5		0.886455	0.383032
135		0.885685	0.381572
135.5		0.885365	0.383068
136		0.88399	0.383503
136.5		0.883522	0.388231
137		0.883275	0.38828
137.5		0.881527	0.386884
138		0.881456	0.392716
138.5		0.883547	0.393676
139		0.878322	0.39723
139.5		0.879797	0.394901
140		0.879126	0.39706
140.5		0.879812	0.402492
141		0.879225	0.400591
141.5		0.927144	0.401706
142			0.407814
142.5			0.403095
143			0.407185
143.5			0.405086
144			0.408217
144.5			0.411074
145			0.416216
145.5			0.418369
146			0.418089
146.5			0.417608
147			0.418409
147.5			0.42611
148			0.42379
148.5			0.42404
149			0.430896
149.5			0.436328
150			0.432452
150.5			0.433666

151			0.439928
151.5			0.43849
152			0.442936
152.5			0.444908
153			0.444946
153.5			0.444836
154			0.446449
154.5			0.446359
155			0.449674
155.5			0.452446
156			0.456079
156.5			0.457958
157			0.455151
157.5			0.460356
158			0.45703
158.5			0.462778
159			0.463769
159.5			0.463503
160			0.467122
160.5			0.465682
161			0.467388
161.5			0.472686
162			0.473563
162.5			0.473635
163			0.479125
163.5			0.478536
164			0.481427
164.5			0.485546
165			0.480257
165.5			0.482793
166			0.486868
166.5			0.486916
167			0.490252
167.5			0.490076
168			0.489979
168.5			0.492173
169			0.49489
169.5			0.497389
170			0.499382
170.5			0.496652
171			0.497451
171.5			0.50216
172			0.500543
172.5			0.499988

173			0.50317
173.5			0.505374
174			0.507579
174.5			0.510959
175			0.510605
175.5			0.508213
176			0.508877
176.5			0.513105
177			0.506831
177.5			0.510995
178			0.518347
178.5			0.514159
179			0.520764
179.5			0.518334
180			0.521336
180.5			0.525994
181			0.52323
181.5			0.524194
182			0.52502
182.5			0.52506
183			0.52899
183.5			0.532208
184			0.534611
184.5			0.531478
185			0.533701
185.5			0.535653
186			0.534911
186.5			0.539343
187			0.539405
187.5			0.540293
188			0.544081
188.5			0.542115
189			0.547554
189.5			0.54582
190			0.548918
190.5			0.548301
191			0.55
191.5			0.551953
192			0.553228
192.5			0.551335
193			0.557617
193.5			0.552268
194			0.554789
194.5			0.559597

195			0.557482
195.5			0.558379
196			0.558589
196.5			0.564473
197			0.564869
197.5			0.56537
198			0.569083
198.5			0.568214
199			0.568488
199.5			0.570423
200			0.572546
200.5			0.570997
201			0.570086
201.5			0.573584
202			0.577284
202.5			0.583088
203			0.581373
203.5			0.577357
204			0.582542
204.5			0.582712
205			0.585565
205.5			0.58628
206			0.586758
206.5			0.587062
207			0.594168
207.5			0.590982
208			0.592002
208.5			0.591457
209			0.595222
209.5			0.598304
210			0.599218
210.5			0.597826
211			0.598563
211.5			0.602164
212			0.604864
212.5			0.60786
213			0.606604
213.5			0.607645
214			0.611876
214.5			0.611978
215			0.610912
215.5			0.614455
216			0.615684
216.5			0.614503

217			0.614662
217.5			0.619256
218			0.616146
218.5			0.620935
219			0.624613
219.5			0.62381
220			0.624311
220.5			0.628028
221			0.629654
221.5			0.629406
222			0.630789
222.5			0.630973
223			0.637618
223.5			0.632975
224			0.636513
224.5			0.637659
225			0.639786
225.5			0.641517
226			0.638922
226.5			0.645744
227			0.642167
227.5			0.645202
228			0.645819
228.5			0.649187
229			0.646788
229.5			0.651649
230			0.652787
230.5			0.653997
231			0.653921
231.5			0.656235
232			0.659938
232.5			0.660333
233			0.658946
233.5			0.662342
234			0.662704
234.5			0.664461
235			0.665734
235.5			0.668679
236			0.668537
236.5			0.671264
237			0.66858
237.5			0.670829
238			0.670624
238.5			0.671671

239			0.673155
239.5			0.676089
240			0.671572
240.5			0.674316
241			0.676093
241.5			0.678077
242			0.676508
242.5			0.681882
243			0.680159
243.5			0.681145
244			0.67991
244.5			0.682256
245			0.682445
245.5			0.680492
246			0.683571
246.5			0.683241
247			0.682376
247.5			0.685192
248			0.687001
248.5			0.687076
249			0.68641
249.5			0.690784
250			0.689959
250.5			0.686535
251			0.686038
251.5			0.688577
252			0.690118
252.5			0.687747
253			0.687939
253.5			0.687552
254			0.690226
254.5			0.688743
255			0.690438
255.5			0.690954
256			0.691735
256.5			0.690138
257			0.688742
257.5			0.694311
258			0.690111
258.5			0.691862
259			0.690775
259.5			0.693458
260			0.692676
260.5			0.692902

261			0.693403
261.5			0.693639
262			0.694831
262.5			0.694016
263			0.694803
263.5			0.695173
264			0.694337
264.5			0.694442
265			0.696283
265.5			0.698081
266			0.692474
266.5			0.694492
267			0.694601
267.5			0.697706
268			0.69601
268.5			0.69632
269			0.694855
269.5			0.698805
270			0.695727
270.5			0.70101
271			0.695262
271.5			0.701334
272			0.698804
272.5			0.69832
273			0.695839
273.5			0.698084
274			0.696152
274.5			0.696931
275			0.699962
275.5			0.699229
276			0.699051
276.5			0.698786
277			0.700679
277.5			0.699595
278			0.69921
278.5			0.702331
279			0.69933
279.5			0.698529
280			0.699037
280.5			0.698836
281			0.697031
281.5			0.699969
282			0.696932
282.5			0.702383

283			0.701958
283.5			0.699912
284			0.69825
284.5			0.699581
285			0.700582
285.5			0.700933
286			0.701279
286.5			0.699797
287			0.702935
287.5			0.698636
288			0.70295
288.5			0.701601
289			0.701522
289.5			0.700883
290			0.701966
290.5			0.699992
291			0.702415
291.5			0.701221
292			0.699002
292.5			0.701838
293			0.702742
293.5			0.699624
294			0.700587
294.5			0.704473
295			0.702452
295.5			0.706084
296			0.699954
296.5			0.704615
297			0.701319
297.5			0.701509
298			0.700278
298.5			0.701638
299			0.704114
299.5			0.7039
300			0.702472
300.5			0.705669
301			0.70509
301.5			0.702839
302			0.70372
302.5			0.702316
303			0.701571
303.5			0.704277
304			0.704583
304.5			0.702586

305			0.704176
305.5			0.702858
306			0.705117
306.5			0.704834
307			0.704232
307.5			0.703339
308			0.705432
308.5			0.704521
309			0.708119
309.5			0.705784
310			0.706078
310.5			0.705648
311			0.706976
311.5			0.704356
312			0.705071
312.5			0.704254
313			0.706247
313.5			0.703379
314			0.706771
314.5			0.704742
315			0.709124
315.5			0.708889
316			0.705951
316.5			0.706257
317			0.705522
317.5			0.705823
318			0.708692
318.5			0.704433
319			0.705717
319.5			0.706816
320			0.705527
320.5			0.705502
321			0.705417
321.5			0.70413
322			0.708059
322.5			0.705008
323			0.705982
323.5			0.704963
324			0.704638
324.5			0.709475
325			0.705818
325.5			0.704844
326			0.706436
326.5			0.70912

327			0.70659
327.5			0.707644
328			0.708328
328.5			0.707986
329			0.710593
329.5			0.70944
330			0.702891
330.5			0.708278
331			0.704194
331.5			0.710363
332			0.707335
332.5			0.709819
333			0.708522
333.5			0.710366
334			0.707266
334.5			0.709532
335			0.709345
335.5			0.709503
336			0.705367
336.5			0.707829
337			0.708652
337.5			0.71023
338			0.708762
338.5			0.705643
339			0.707938
339.5			0.709927
340			0.708287
340.5			0.70966
341			0.710014
341.5			0.707258
342			0.708725
342.5			0.710924
343			0.709908
343.5			0.710645
344			0.707366
344.5			0.710459
345			0.712255
345.5			0.710278
346			0.708488
346.5			0.711891
347			0.70958
347.5			0.711281
348			0.709695
348.5			0.711022

349			0.711758
349.5			0.71039
350			0.709687
350.5			0.712461
351			0.709357
351.5			0.712127
352			0.711
352.5			0.712465
353			0.712509
353.5			0.708712
354			0.712615
354.5			0.711687
355			0.714892
355.5			0.714347
356			0.713901
356.5			0.711226
357			0.711647
357.5			0.713444
358			0.711277
358.5			0.714777
359			0.711966
359.5			0.711536
360			0.711453
360.5			0.713068
361			0.712818
361.5			0.712304
362			0.71515
362.5			0.711486
363			0.709658
363.5			0.712956
364			0.712072

Appendix 2. Bottle number and outlet CO₂ volume percentages obtained in the gas residence time in alkaline solution experiment.

Time minutes	One bottle CO ₂ ppm levels	Two bottle CO ₂ ppm levels	Time minutes	Three bottle CO ₂ ppm levels	Four bottle CO ₂ ppm levels	Five bottle CO ₂ ppm levels	Six bottle CO ₂ ppm levels
1	3887.16	953.296	0	604.51	87.4748	15.994	7.3
1.5	4026.28	846.19	16	605.64	139.462	32.334	2.085
2	3974.67	802.853	32	611.71	149.73	34.64	2.085
2.5	3929.32	734.561	48	689.77	148.36	35.8	2.085
3	3971.46	724.999	64	711.763	157.86	48.725	2.085
3.5	3911.97	679.066	80	748.94	163.401	51.202	2.085
4	3903.03	672.027	96	773.12	178.22	62.593	2.085
4.5	3886.43	626.515					
5	3918.66	629.223					
5.5	3914.57	593.513					
6	3870.61	588.609					
6.5	3864.01	552.828					
7	3835.51	554.643					
7.5	3810.51	518.98					
8	3821.97	489.321					
8.5	3897.24	509.358					
9	3767.84	495.225					
9.5	3845.2	487.99					
10	3838.02	462.75					
10.5	3813.08	466.699					
11	3769.05	480.105					
11.5	3833.48	445.149					
12	3796.48	439.966					
12.5	3792.16	409.002					
13	3783.79	410.886					
13.5	3792.69	422.282					
14	3818.93	396.717					
14.5	3781.09	383.034					
15	3808.86	391.474					
15.5	3837.61	375.16					
16	3805.04	375.021					
16.5	3811.8	350.847					
17	3786.78	361.463					
17.5	3831.03	350.988					
18	3794.18	353.532					

18.5	3769.53	331.723
19	3807.86	336.928
19.5	3872.2	331.795
20	3910.21	339.087
20.5	3874.3	318.208
21	3837.14	305.062
21.5	3822.75	302.6
22	3809.45	295.947
22.5	3893.59	289.86
23	3866.13	302.734
23.5	3830.83	288.829
24	3902.39	297.607
24.5	3868.73	282.367
25	3884.38	283.81
25.5	3887.42	276.762
26	3921.44	272.272
26.5	3957.14	257.777
27	3942.5	269.792
27.5	3927.04	267.219
28	3932.55	261.135
28.5	3954.79	250.495
29	3982.99	230.238
29.5	3961.58	245.421
30	3987.99	240.893
30.5	4032.71	237.67
31	4053.77	238.73
31.5	4026.72	241.342
32	4083.36	225.373
32.5	4085.02	222.126
33	3997.7	
33.5	4006.83	
34	3992.5	
34.5	3833.9	
35	3701.39	
35.5	3514.04	
36	3306.05	

Appendix 3. Outlet methane volume percentages obtained in high alkaline concentrations for methane absorption experiment.

Time	Methane outlet
0	25.0981
0.5	25.142
1	25.169
1.5	25.1836
2	25.1857
2.5	25.1947
3	23.4064
3.5	11.9959
4	11.7728
4.5	17.818
5	21.6337
5.5	23.4929
6	24.3985
6.5	24.839
7	25.0681
7.5	25.1995
8	25.265
8.5	25.306
9	25.3277
9.5	25.3368
10	25.3464
10.5	25.3524
11	25.3557
11.5	25.3589
12	25.3609
12.5	25.362
13	25.3604
13.5	25.3608
14	25.3616
14.5	25.3615
15	25.3612
15.5	25.3624
16	25.3607
16.5	25.3635
17	25.3631
17.5	25.3643
18	25.3618
18.5	25.3466
19	25.3523
19.5	25.3553
20	25.3576
20.5	25.3526

21	25.3595
21.5	25.3579
22	25.358
22.5	25.3597
23	25.3579