Abstract
Gasification is considered as one of the most attractive conversion technologies, because the product gas from the process serves as a building block for several industrial applications. However, the use of biomass as a fuel in the gasification process offers a carbon neutral fuel that will alleviate the continuing use of fossil fuels sources.

This study was done to evaluate the possible applications of syngas originating from biomass gasification, as a follow up to the earlier biomass gasification research of the HighBio project. The syngas from the gasification process is generally produced in a gasifier. An overview of the different type of gasifiers for biomass gasification that include updraft, downdraft, crossdraft, entrained-flow and plasma gasifiers was presented.

The syngas can be utilized in the generation of power, heat, fuels and chemicals. A detailed overview of the promising applications of the syngas in Fischer-Tropsch synthesis, hydrogen production, ammonia synthesis, hydroformylation of olefins, and syngas fermentation was also given.

However, for these applications, a high degree of treatment and conditioning of the syngas is required. The treatment is usually carried out to remove undesirable impurities, while the conditioning of the gas is done to get the right H\textsubscript{2} to CO ratio for further applications of the syngas.

Raw syngas from gasification processes can contains also impurities such as solid particulates, inorganic and organic impurities, which have to be removed. However, CO\textsubscript{2} is one of the major by-products in a gasification process. The removal of CO\textsubscript{2} is desirable in order to reduce the CO\textsubscript{2} emissions or to meet the downstream process requirement in relation to size and costs. Absorption processes are the most developed techniques in the separation of CO\textsubscript{2} in the industries. However, other techniques such as adsorption, membrane separation, and chemical-looping combustion have recently gained interest.

Moreover, two MFI-types zeolite membranes (ZSM5-I and ZSM5-II) were tested in the separation of CO\textsubscript{2} from CO\textsubscript{2}/N\textsubscript{2} mixtures in a laboratory scale experiments. Separation factor, gas permeability and CO\textsubscript{2} permeate flux were the parameters used to determine the membrane performance. The highest membrane performances of the feed gas compositions were achieved with low CO\textsubscript{2} gas composition, and at the low temperature separation experiments.

However, in order to achieve high recovery and purity of CO\textsubscript{2}, the separation experiment of the HighBio CO\textsubscript{2}/N\textsubscript{2} feed composition using the ZSM5 zeolite membrane was evaluated at low temperature and constant feed and permeate pressures of 6 bar and 1 bar respectively. Based on the analysis, it is suggested that 6 successive membrane modules should be employed. Further investigations that incorporate other product gas compositions from biomass gasification, as well as the study of other type of inorganic membranes more suitable to CO\textsubscript{2}/N\textsubscript{2} separation processes are highly recommended. The economic analysis of the multi-stage ZSM5 zeolite membrane separation could be also another interesting study.
Acknowledgement

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3
Abbreviations

CA Carbon Anhydrase
CFB Circulating-Fluidized-Bed
CHP Combined-Heat and Power
CLC Chemical-Looping Combustion
DEA Diethanolamine
DEPG Dimethyl Ether of Polyethylene Glycol
DME Dimethyl Ether
EFG Entrained-Flow Gasifier
ESPs Electrostatic Precipitators
ETC Energy Technology Centre
FAO Food and Agricultural Organization
FT Fischer-Tropsch
FTMs Facilitated Transport Membranes
IC Internal Combustion
IEA International Energy Agency
IGCC Integrated Gasification Combined-Cycle
ILs Ionic Liquids
IPCC Intergovernmental Panel on Climate Change
MAE Methylalminoethanol
MEA Monoethanolamine
MMMs Mixed Matrix Membranes
MOFs Metal-Organic Frameworks
NETL National Energy Technology Laboratory
NMP N-Methyl-2-Pyrrolidone
NREL National Renewable Energy Laboratory
NTP Normal Temperature and Pressure
PC Propylene Carbonate
PI Pressure Indicator
PIC Pressure Indicator Control
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT</td>
<td>Pressure Indicator</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure-Swing Adsorption</td>
</tr>
<tr>
<td>PZ</td>
<td>Piperazine</td>
</tr>
<tr>
<td>SASOL</td>
<td>South Africa Synthetic Oil</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature and Pressure</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethanolamine</td>
</tr>
<tr>
<td>TI</td>
<td>Temperature Indicator</td>
</tr>
<tr>
<td>TSA</td>
<td>Thermal-Swing Adsorption</td>
</tr>
<tr>
<td>WGS</td>
<td>Water-Gas Shift</td>
</tr>
</tbody>
</table>
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Introduction

One of the greatest challenges in the 21st century has been how to correlate the ever increasing population growth, emission reduction and energy-demand. This is clearly visible to the several projections reported to that effect. Over the years and at the present, fossil fuels are the dominant source for energy production and use across the globe. However, concerns on fluctuating oil prices, awareness of limited oil reserves, energy security, and greenhouse gas emissions mostly from fossil fuel based sources for energy production and use has promoted a search for alternative sources of energy. This has now become a topic of discussion among relevant stakeholders in the present century.

According to the projection reported by Intergovernmental Panel on Climate Change, unless current trends in energy production and use have been revisited, the increased concentration of greenhouse gases in the atmosphere could ultimately disrupt the societal, economic development and environmental consequences of both the present and future generations (IPCC 2000). This concern has led to the massive endorsement that many of the world countries gave to the United Nation Kyoto Protocol. The notion has reopened interest in renewable energy sources as an alternative to the use of fossil fuels for the production and use of energy. While other renewable energy sources such as solar and wind have their limitations for the above mentioned goal, biomass on the hand, is the only available renewable carbon source that is foreseen to replace fossil fuels both in the production of electricity, heat, fuels and chemicals. There are number of technological routes of converting biomass into electricity, heat, fuels and chemicals. However, gasification is considered as one of the most attractive conversion technologies, because the product gas from the process serves as a building block for many industrial applications.

Gasification process converts carbon feedstock into carbon monoxide, hydrogen, carbon dioxide and traces of other impurities depending on the fuel source. The mixture is otherwise known as syngas, which itself is a fuel that provides a number of applications in industrial processes. For the purpose of this research project, the term syngas is used when referring to the wood gas. However, in keeping with the sustainability and downstream process requirements, it is required that the product gas should be treated and conditioned (Basu 2010 304). One such requirement is the removal of carbon dioxide, an important greenhouse gas, which also does not have any useful heating
value in the downstream processes. Recent advances in the capture of carbon dioxide envisaged in the utilization of the captured carbon dioxide for further uses, such as in other chemical syntheses, or enrichment in greenhouses for plant growth. Therefore, this study focuses on the recovery of carbon dioxide from the gasifier product gas, as part of the HighBio2 project in which the University of Oulu is a partner. Further use of the captured CO₂ is however not covered and is therefore beyond the scope of this study.
THEORY PART

1. Biomass Gasification Process

This section draws heavily on (Basu 2010) to highlight the biomass gasification process. Gasification can be defined as the thermochemical conversion of carbonaceous materials into a mixture of CO, H₂, and CO₂, under low oxygen levels. The mixture is otherwise known as syngas. It is the main building block for many useful industrial applications due to its high energy density. Biomass for gasification can be sourced from agricultural residues, forestry or agro-industries. The main parameters for the process are temperature, the gasifier type and the gasifying medium. Usually, the biomass fuel is initially heated to undergo thermal degradation. The gasification process is generally an exothermic process. Therefore, the energy need in the process is acquired from the exothermic reactions occurring inside the gasifier. Depending on the biomass source, the process steps consist of drying, thermal decomposition, partial combustion and the decomposition of the products. In each of these process steps, a number of reactions take place. The reactions are made up of but not limited to, carbonation, oxidation, shift, methanation and steam reforming reactions.

The moisture content in biomass fuel is usually high. Therefore, the biomass fuel has to be pre-dried in order to remove traces of moisture before it is fed into the gasifier. However, the final drying of biomass fuel is often done in the gasifier. As a rule of thumb for the final drying of biomass, the temperature in the gasifier should be more than 100˚C. However, dry biomass with moisture content between 10-20% is often used in a gasification process. After drying, the biomass undergoes pyrolysis. The pyrolysis is an endothermic process. During the pyrolysis, large complex molecules are breakdown into smaller units at the temperature range of 300-650˚C. The process chemistry of this process is represented in Eq. (1) below.

\[ C_nH_mO_p \text{(Biomass)} \rightarrow \Sigma_{\text{liquid}} C_xH_yO_z + \Sigma_{\text{gas}} C_aH_bO_c + H_2O + C \text{ (Char)}, \]  

(1)

where \( n, m, p, x, y, z, a, b, c \) vary from 1-6 depending on the feedstock, heating rate and the final temperature reached in the gasifier during pyrolysis.
Pyrolysis process can be divided into slow and fast pyrolysis. The fast pyrolysis requires faster heating rate than the slow pyrolysis. However, char is normally produced in slow pyrolysis, while bio-oil is often produced in the fast pyrolysis. (Basu 2010 65, 71 & 117-120) The steps of gasification can be viewed in Figure 1.

Figure 1. Steps in gasification process (Adapted from Basu 2010 119).

The pyrolysis process is followed by char gasification reactions. In this step, a series of reactions take place between char and the surrounding gases. The rate at which char reacts depends on its reactivity and the potential of the gasifying medium. However, the reaction between char and oxygen takes place at faster rate compared to char reaction with steam or carbon dioxide (Eq. 2). In general, the use of pure oxygen as gasifying medium results in higher heating value due to the absent of nitrogen. Char-steam reaction on the other hand yields CO and H₂, but the reaction is quite slow than that of char and oxygen. The reaction between char and carbon dioxide, which is otherwise known as a Boudouard reaction (Eq. 3), is also slower than both char-oxygen and char-steam reactions. Further to the Boudouard reaction, is a water-gas reaction (Eq. 4). The water-gas reaction takes place at a faster rate. The reaction favors the formation of
hydrogen in contrast to carbon monoxide. This is however, the initial stage for the formation of a syngas mixture. However, the reaction between char and hydrogen (Eq. 5), which takes place at a slower rate is undesirable unless the production of synthetic natural gas (SNG) is required. Char combustion reaction is exothermic in nature. The reaction provides the heat necessary for heating, drying and pyrolysis processes in the gasifier. (Basu 2010 122-126)

**Table 1. Main reactions in the gasification process**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction heat [kJ/mol]</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + 0.5O₂ → CO</td>
<td>−111</td>
<td>(2)</td>
</tr>
<tr>
<td>C + CO₂ ↔ 2CO</td>
<td>+172</td>
<td>(3)</td>
</tr>
<tr>
<td>C + H₂O ↔ CO + H₂</td>
<td>+131</td>
<td>(4)</td>
</tr>
<tr>
<td>C + 2H₂ ↔ CH₄</td>
<td>−74.8</td>
<td>(5)</td>
</tr>
<tr>
<td>CH₄ + H₂O →[Catalyst] CO + 3H₂</td>
<td>+206</td>
<td>(steam reforming) (6)</td>
</tr>
<tr>
<td>CH₄ + CO₂ →[Catalyst] 2CO + 2H₂</td>
<td>+247</td>
<td>(dry reforming) (7)</td>
</tr>
</tbody>
</table>

Furthermore, a catalytic gasification process employs a catalyst that promotes the formation of the syngas mixture. The simplest reactions of this nature are the steam reforming reaction (Eq. 6) and the catalytic carbon dioxide reforming of methane (Eq. 7). (Basu 2010 128-129)

### 1.1. Gasifier Types

The gasification takes place in a reactor otherwise known as a gasifier. The design of the gasifier is an essential aspect that is influenced by the type of feedstock and its properties, the desired gas quality and capacity requirement. In general, there are three stages in the design of a gasifier. These include process synthesis and preliminary sizing, optimization of the design and detailed mechanical design of the equipment (Basu 2010 167). The main gasifier types currently in use are updraft, downdraft, crossdraft, fluidized bed and circulating fluidized bed gasifiers.

#### 1.1.1. Updraft Gasifiers

Updraft is the oldest and simplest form of a gasifier (Fig. 2). As the name implies, in the updraft gasifiers the gasifying medium moves upward while the fuel flows downward.
In the updraft gasifier, the fuel and the gasifying medium flow counter-currently through the gasifier. This enables the product gas to leave from the top of the gasifier and at a low temperature (Rezaiyan and Cheremisionoff 2005 124; FAO 1986 22; McKendry 2002).

Prior to contact with the fuel, the gasifying medium is slightly preheated and as it enters the bottom of the bed it comes in contact with hot ash and unconverted chars. Combustion takes place near the grate, which is followed by a reduction reaction higher up in the gasifier. Due to heat transfer from the lower part of the gasifier, the heating and pyrolysis process take place in the upper part of the gasifier. In the gas stream there are tars and volatiles formed in the process. The ash is however removed from the bottom of the gasifier (FAO 1986 22; McKendry 2002).

The major advantages of this type of a gasifier are its suitability for high ash and high moisture biomass and low-volatile fuels. In addition, high cold-gas efficiency can be achieved with the gasifier due to the effective utilization of the combustion heat. (Basu 2010 170-171; FAO 1986 22) However, the major drawbacks of the updraft gasifier are, possible channeling in the equipment, (FAO 1986 22), high sensitivity to tar and
moisture content in the fuel, poor reaction capacity with heavy gas, and longer start up time especially in IC engines (Rajvanshi 1986). Updraft gasifiers are commercialized in small and large units. Typically the large units are used in the production of gasoline from coal (Basu 2010 171).

1.1.2. Downdraft Gasifiers

Downdraft or co-current gasifiers have been designed to alleviate the problems of tar formation. In this type of a gasifier, air is introduced at or above an oxidation zone and the product gas is removed at the bottom of the gasifier. In a downdraft gasifier (Fig. 3), the fuel and product gas flow in the same direction. The products pass through a glowing bed typically made up of charcoal. The products are rarely converted into permanent gases like hydrogen, carbon dioxide, carbon monoxide and methane. Depending on the temperature, near or complete tar cracking can be achieved as the product gas exits of high-temperature zone. Low tar formations and shorter ignition time make it suitable for use with internal-combustion engines. These facts are generally the major advantages of a downdraft gasifier. (FAO 1986 23-24)

Figure 3. Updraft gasifier (Adapted from FAO 1986 23).
Despite these benefits, downdraft gasifiers are associated with some drawbacks. The main drawbacks of the gasifier are that it is unsuitable for small particle size fuels, there is a restriction on the moisture content, large amount of ash and dust is formed, as well as low gasification temperature resulting from high temperature exit of the product gas (FAO 1986 24; Rajvanshi 1986).

1.1.3. Crossdraft Gasifier

Crossdraft gasifiers are typically used in char gasification especially when the char has low-ash content (FAO 1986 24; Basu 2010 176). In crossdraft gasifiers, the gas flow is perpendicular to the fuel flow. High velocity air is injected through a nozzle from the side and fuel flows from the top of the gasifier. The products are then released from the side of the wall at opposite to the entry point of air. In one of the zones, high temperature resulting from charcoal gasification promotes combustion of the charcoal, which is converted to CO at the downstream in the other zone. The crossdraft gasifiers find applications in small-scale biomass units. The major advantages of this gasifier are the faster response time than any other moving-bed gasifier, short start-up time, low tar production, as well as simple gas cleaning system (Basu 2010, 176, FAO 1986 24). However, the major drawbacks of the crossdraft gasifiers are high pressure drop and difficulty with high-ash or high-tar containing fuels (Rajvanshi 1986; FAO 1986 24; Basu 2010 176). However, with the appropriate design, crossdraft gasifier can handle a fuel with high-moisture content (Basu 2010 177). A schematic figure of a crossdraft gasifier is shown in Figure 4.
1.1.4. Fluidized-bed Gasifiers

Fluidized bed gasifiers are designed to alleviate the problems of slagging. In addition, they have less bunker flow and pressure drops than associated with the downdraft and updraft gasifiers (FAO 1986 24). Fluidized bed gasifiers provide excellent mixing and temperature uniformity. These are enabled by injecting air through the bed material at desirable velocity in order to keep the bed in suspension (Basu 2010 177; FAO 1986 24). Usually the bed is externally heated to a high temperature before the fuel is introduced. As the fuel is fed from the bottom of the gasifier, rapid mixing with the bed material enhances front heat up to the bed temperature. (FAO 1986 24)

Fluidized bed gasifiers are divided into bubbling and circulating gasifiers. The bubbling gasifiers (Fig. 5) are considered to be suitable for biomass fuel due to the medium-size of the gasifiers. In its operation, the bed is fluidized with the gasification medium, and the ash generated is drained from the bottom of the bed. The gasification medium is initially supplied to maintain the desired fluidized bed temperature. The second supply is done above the bed to convert unreacted char and hydrocarbons into useful gas. Depending on the operating conditions, bubbling fluidized-bed gasifiers can be further classified into high-temperature, low-temperature, atmospheric or elevated pressure bubbling fluidized gasifiers. (Basu 2010, 177-178)
Circulating fluidized-bed gasifier (CFB) (Fig. 6) on the other hand, combines the advantages of a stationary fluid bed and a transport reactor. The size and shape of the feedstock has little or no influence in the operation with CFB. This is however beneficial in the gasification of biomass and waste materials. CFB is characterized by good gas and solids mixing due to the high-slip velocity that enhance excellent heat and mass transfer. In CFB operations, small particles are easily consumed at a faster rate. The large particles are slowly breakdown into smaller units before the external recycling. (Higman and van der Burgt 2003 105) CFB is one of the commercialized gasifiers with the world’s largest been the 140 MW coal-biomass gasification plant that was inaugurated in March 2013 at Vaasa, Finland.
Figure 6. Circulating fluidized-bed gasifier (Adapted with permission from Higman and van der Burgt 2003 106).

1.1.5. Entrained-Flow Gasifiers

Gasification with the entrained-flow gasifiers is one of the most developed gasification technology. The entrained-flow gasifiers (Fig. 7) utilize coal, petroleum coke and refinery products as feedstock. In addition, they are suitable for IGCC applications (Higman and van der Burgt 2003 110).
The entrained-flow gasification operates with smaller fuel particles under a high temperature compared to the previously presented gasifiers. The particle sizes and the temperature promote high carbon conversion, and can enhance the production of syngas with very low contents of tar and other hydrocarbons (Marklund and Öhrman 2011). This type of gasifiers are known to work by dragging the fuel particles along with the gas stream thereby providing a short residence time (Van der Drift et al. 2004; Higman and van der Burgt 2003 85).

Entrained-flow gasifiers can be operated in a pressure range of 20-70 bar, and with fuel particles with a diameter of up to 100 µm (Higman and van der Burgt, 2003 85 & 110). Entrained flow gasification is a well proven technology for most type of coal. However, the main exception of this is coal with high moisture or ash content (Basu 2010 186). The entrained-flow gasification of biomass is very challenging, but for complete destruction of tar, which is associated with biomass fuels, there are significant research projects going on across the globe. For instance, at ETC, located in Piteå (Sweden), a partner in the HighBio project, high pressure entrained-flow biomass gasification is
investigated in a pilot plant. Other challenges associated with the entrained-flow gasification are the processing and supply of fuel, and control of slag formation (Marklund and Öhrman 2011).

1.1.6. Plasma Gasifiers

Plasma gasifiers are designed mainly to utilize municipal solid and organic wastes into syngas and slag. The operation principle of the plasma gasifier (Fig. 8) is based on the usage of a plasma torch. The torch is powered by electric arc that ionizes the gas and catalyzes organic matter into syngas and solid waste (Moustakas et al. 2005). The working temperature in the plasma gasifiers is extremely high being enough to decompose the waste material into smaller particles. The high temperature and longer residence time in the reactor, promotes tar cracking as well as the destruction of harmful products. However, the main drawback with the plasma gasification is the short lifespan of the reactor liner. This is attributed to the high temperature in the process, as well as the presence of chlorine in the waste materials (Basu 2010 192).

![Figure 8. Plasma gasification (Adapted from Basu 2010 191).]
1.2. Gasification Process Products

Depending on the fuel used, a gasification process yields a mixture with different proportions of CO, H₂ CO₂, CH₄, hydrocarbons, tar and traces of other impurities. The derived syngas compositions depends among other things of the feedstock used, the design of the gasifier, temperature, pressure, the gasifying medium and the heat losses from the gasifier. The heat losses from the gasifier signify that more heat has to be generated by combustion. Hence more C and H is converted to CO₂ and H₂O, thereby requiring more oxygen. This in turn means in practice that the product gas is diluted by N₂. In coal gasification, significant amounts of H₂S and NH₃ are expected to form due to the presence of sulfur and nitrogen in the fuel. On the other hand, gasification of a biomass fuel results in the formation of tar. An example of the product gas composition of a gasifier is shown in Table 2.

Table 2. Typical composition and concentrations of the product gas from a downdraft biomass gasifier (Muilu and Pieniniemi 2011).

<table>
<thead>
<tr>
<th>Product gas component</th>
<th>vol.%</th>
<th>g/Nm³ (STP 0°C, 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>15</td>
<td>187</td>
</tr>
<tr>
<td>CO</td>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.5</td>
<td>18</td>
</tr>
<tr>
<td>CO₂</td>
<td>15</td>
<td>295</td>
</tr>
<tr>
<td>N₂</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Other gaseous compounds</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>
2. Utilization of Syngas

Syngas can be used in several applications like the generation of power, heat, fuels and chemicals. It can be also used to generate heat and electricity in a combined-heat and power plant, in an IGCC plant or in a fuel cell. Further to that, syngas can be also utilized in Fischer-Tropsch synthesis, in the production of hydrogen and methanol, ammonia synthesis, hydroformylation of olefins, and syngas fermentation. In these applications, it is very essential that the syngas is well-treated and conditioned. Figure 9 below depicts the possible end-use applications of the derived-syngas from a gasification process.

Figure 9. End-use applications of derived-syngas (Adapted from Higman and van der Burgt 2003 232).
2.1. Power Generation

Generation of power from biomass such as wood provides both technical and economical option for the reduction of CO$_2$ emission. Biomass-derived syngas can be combusted in an engine in order to generate heat and electricity. In many of the Nordic countries, biomass-cofiring has been in practice due to the relatively high efficiency of the process. The major sources of biomass in these countries are different wood species and residues from forestry. A typical example of biomass co-firing is the 160 MW Foster Wheeler’s Circulating Fluidized gasifier plant in Lahti Finland. However, the major technical challenges with biomass co-firing are the deposition of ash and corrosion in the biomass-fuelled boiler (Shao et al. 2012).

Recently, interest has concentrated on the IGCC for the generation of electricity. The efficiency in an IGCC process is higher compared to the one of a combustion plant. In the IGCC plants, clean gas can be produced and combusted in a turbine to generate heat and electricity. Additionally, the exhaust gas temperature in the IGCC plant is sufficient enough to drive a conventional steam turbine. Therefore, additional electricity can be also generated. The emission of compounds such as SO$_2$, NO$_x$ and particulates are easily controlled in the IGCC process. (Rezaiyan and Cheremisionoff 2005 272-274) A typical example for the application of the IGCC is the plant located in Värnamo Sweden. The IGCC plant in Värnamo has a capacity of producing 9 and 6 MW of heat and electricity respectively. However, the major drawbacks with IGCC processes are the high investment cost (Mondal et al. 2012) and the technical complexity of the process (Damen et al. 2006).

Another possible application of biomass-derived syngas components for the generation of electricity is in a fuel cell. In the fuel cell an electrochemical reaction occurs where H$_2$ is burnt to produce electricity directly. Hydrogen, a major component of the syngas, can be burnt in a fuel cell with a high efficiency (Rezaian and Cheremisionoff 2005 272). Other components in the product gas of a gasifier such as CH$_4$ can be used to produce additional H$_2$ for a fuel cell via steam reforming.

2.2. Transportation Fuels

Transportation is one of the dominant sectors in energy consumption with about 2370 Mtoe consumed in 2010 (IEA 2012). The majority of the consumption comes from the fossil fuel based sources that are associated with serious negative impacts on the
environment. In contrast to this trend, biomass gasification provides an alternative to the production and use of fuels for transport activities with negligible carbon emissions. This has made biomass as an attractive fuel source for the production of transportation fuels such as liquid hydrocarbons, ethanol and methanol.

2.2.1. Fischer-Tropsch Synthesis

Fischer-Tropsch (FT) was developed in 1920s by the German scientists Franz Fischer and Hans Tropsch. In the FT synthesis, syngas is catalytically converted into liquid hydrocarbons and chemicals. Hence, the process can be categorized as a Gas-to-Liquids fuel process. In the FT process syngas produced from a gasification process undergoes cleaning to meet the FT synthesis requirements. The syngas is then further utilized in the FT catalytic reactor to produce high-quality diesel oil (Hu et al. 2012). The process flowsheet of FT synthesis is depicted in Figure 10.

![Figure 10. Flowsheet for biomass Fisher-Tropsch process (Adapted from Hu et al. 2012).](image)

For the FT synthesis, it is ideal to have H$_2$/CO ratio of unity, which is ideal for the FT catalysts. However, reaching the target ratio is dependent both on the feedstock and the gasification conditions. (Basu 2010 313) In most cases, biomass gasification leads to the lower H$_2$/CO ratio. Hence, the water shift reaction is required to adjust the H$_2$/CO ratio (Tijmensen 2002). The FT reaction

\[
\begin{align*}
nCO + 2nH_2 \xrightarrow{\text{Catalyst}} (CH_2)_n + nH_2O + \text{Heat}
\end{align*}
\]  

is exothermic and takes place in the temperature range of 200-350°C. The composition of the produced diesel oil is similar to that of petrol diesel (Basu 2010 313). This oil can
be blended with petrol diesel or burnt directly in an engine. Furthermore, products such as olefins ranging from C₅ (Boerrigter et al. 2004; Tijmensen et al. 2002) to C₁₀ (Boerrigter et al. 2004; Galvis et al. 2012) can also be produced from synthetic fuels. Many catalysts find application in FT synthesis. The most attractive catalysts for FT synthesis are based on iron and cobalt (Boerrigter et al. 2004; Dry 2002; Tijmensen et al. 2002; Glavis et al. 2012). Compared to the iron based catalysts, the cobalt based catalysts promote higher conversion rate, longer catalyst life and are more reactive in the hydrogenation process. Iron based catalysts on the other hand, possess high degree of sulfur tolerance (Boerrigter et al. 2004). However, these catalysts can be poisoned by impurities such as NH₃, HCN, H₂S, COS (Boerrigter et al. 2004). Additionally, other side reactions such as Boudourd reaction and methanation could lead to the deposition of carbon on the active sites of the catalyst and competitive production of methane respectively (Galvis et al. 2012). In general, the cost of gas purification remains one of the greatest challenges in the FT syntheses (Dry 2002). The world famous FT syntheses are the coal-derived syngas to liquid fuel by SASOL in South Africa, and the natural gas-derived syngas to liquid fuel by Shell in Malaysia (Tijmensen et al. 2002).

2.2.2. Methanol

The market for methanol from gasification was estimated to be about 9% of the world total production. Methanol is an important feedstock for the production of transport fuels and chemicals. It can be produced by the catalytic synthesis of syngas (Eq. 9) (Higman and van der Burgt 2003 239-240) or by steam reforming methane (Eqs. 10-11) (Basu 2010 311)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heat of reaction (kJ/mol)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + 2H₂ → CH₃OH</td>
<td>−91</td>
<td>(9)</td>
</tr>
<tr>
<td>CH₄ + H₂ O → CO + 3H₂</td>
<td>+206</td>
<td>(10)</td>
</tr>
<tr>
<td>CO₂ + 3H₂ → CH₃OH + H₂O</td>
<td>−50</td>
<td>(11)</td>
</tr>
</tbody>
</table>

The methanol synthesis reaction (Eq. 9) is exothermic. Thus the reaction equilibrium is favorable at low temperature (Zhang et al. 2013). Many catalysts based on Cu, Zn, Al and Cr has found applications in methanol synthesis (Basu 2010 310). Figure 11 depicts the process flowsheet for the production of methanol.
As a fuel, methanol is safe, simple alcohol that can be blended with gasoline and ethanol. It has a high octane number suitable for combustion in engines (Bomberg and Cheng 2010). Additionally, methanol derived from syngas can be catalytically dehydrated to produce dimethyl ether (DME). The DME derived from biomass, is an environmentally friendly diesel fuel with low particulate and low nitrous oxide emissions when combusted in an engine, and does not pose any threat to human health (Chemrec 2009). However, the main drawback for the production of methanol as a fuel is the high production cost of the thermochemical plants (Bomberg and Cheng 2010).

### 2.2.3. Mixed Alcohols

Mixed alcohols, ethanol, higher and lower alcohols can be produced by catalytic conversion of syngas (Gerber *et al.* 2007; Higman and van der Burgt 2003). The produced mixed alcohols can further be used as fuels or in chemical syntheses. Several different types of catalysts can be used in the synthesis of mixed alcohols. Some of these catalysts are Rh-based catalysts (Hu *et al.* 2007), Mo-based catalysts (Chen *et al.* 2011), modified methanol synthesis catalysts (Sun and Robert 2003) and modified FT synthesis catalysts (Okabe *et al.* 2001).
2.2.4. Syngas Fermentation

Similar to mixed alcohols synthesis of syngas, biofuels can be produced via syngas fermentation. However, in this process microbes act as a catalyst. Some of the microbes that can be used in the process are Clostridium lyungdahlii, Clostridium autoethanogenum, Acetobacterium woodii, Clostridium carboxidivorans and Peptostreptococcus productus. The major advantage of this process are the possibility to utilize the whole biomass, elimination of complex pre-treatment steps, low enzyme costs, independence of the H₂/CO ratio for bioconversion, possibility to operate the bioreactor at ambient conditions, and the renewability of the process. (Munasinghe and Khanal 2009)

2.3. Chemical Synthesis

Apart from the production of transportation fuels, syngas and its components derived from a gasification process can be used in the syntheses of a number of commodity products. In industries, chemical syntheses of syngas derived from fossil based feed materials are already commercialized. Some of the chemicals that can be produced via chemical synthesis of syngas are ammonia, olefins, hydrogen for refinery, glycerol, and formic acid among others.

2.3.1. Ammonia Synthesis

Ammonia is an important chemical used in the production of fertilizers, nitric acid, plastics, soda ash, synthetic fibers, pulping of wood, as well in petroleum and rubber industries. Ammonia is synthesized using an equilibrium reaction:

\[ \text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3. \]  \hspace{1cm} (12)

The fed nitrogen and hydrogen can be produced by gasification. In the ammonia synthesis, the fed gas is passed through a catalyst bed at a high pressure. The process involves a number of steps. These include the tar and volatiles removal, desulfurization, shift reaction, CO₂ and water removal, as well as the adjustment of the feed N₂/H₂ ratio. (Higman and van der Burgt 2003 232-233) Commercial catalysts iron, chromium, zinc and copper oxides based are often used in ammonia syntheses. In the process, syngas is
passed through a shift reactor, where CO is converted into CO₂ and H₂. CO₂ is then captured in a liquid scrubber. The purified gas is further converted into methane in a methanation reactor. The ammonia synthesis is completed by compressing H₂ with nitrogen at a high pressure (Basu 2010 314).

2.3.2. Glycerol Synthesis

Glycerol is a major by-product in biodiesel production. The compound can be gasified into syngas for the production of electricity as well as several chemical products (Zhou et al. 2008). Glycerol is used in the production of food, cosmetics, paints, pharmaceutics, paper, textiles and leather (Wang et al. 2001). Glycerol is non-toxic, biodegradable and recyclable liquid that can be manufactured from renewable sources. Further to that, it has a high potential as an alternative green solvent for organic reactions (Wolfson et al. 2007). In the process, catalysts play also vital role in the synthesis of glycerol. Metallic based catalysts are the most widely used in the synthesis of glycerol.

2.3.3. Hydroformylation of Olefins

Hydroformylation of olefins is essentially exothermic reaction. In the process, mixture of H₂ and CO is used as a feed to produce aldehydes in the presence of a homogeneous catalyst. The hydroformylation reactions also known as oxo-reaction. It is widely used in petrochemical industries for the catalytic synthesis of Cₙ₊₁ alcohol from Cₙ olefins. The main products of this reaction are aldehydes (Eq. 13).

$$RCH = CH₂ + CO + H₂ \xrightarrow{\text{Catalyst}} RCH₂CH₂CHO + RC(CHO)CH₃$$  \hspace{1cm} (13)

Metal based catalysts are the most widely used for the hydroformylation of olefins in industries (Khan et al. 1990).

2.3.4. Hydrogen

Hydrogen is one of the most important chemicals in industrial processes. It is usually produced via steam reforming. Hydrogen can be used in the hydrogenation and
reduction processes for the following industrial applications (Häussinger et al. 2000 353-361):

- In refineries: hydrogenation processes are often used to increase the hydrogen content of the crude oil fraction
- Coal refinement via hydrogenation, hydrolysis and hydrogenation of coal in gasification processes.
- For the synthetic production of liquids fuels and synthetic natural gas.
- In ammonia synthesis
- In metallurgical industries for the reduction of iron ore.
- In hydrogenation and dehydrogenation of organic synthesis, and
- Inorganic synthesis for the production of hydrogen peroxide, hydrochloric acid and hydroxylamine synthesis.

2.3.5. Derivatives of Carbon Monoxide

Carbon monoxide, another major component of the syngas can be also utilized as a raw material for the production of number of chemicals as depicted in Fig. 12 below. However, the toxicity of carbon monoxide makes it difficult in handling. Hence, pure CO plants should always be located close to the point of use (Higman and van der Burgt 2003 249).
Figure 12: Application of high purity carbon monoxide (Adapted from Higman and van der Burgt 2003 250).
3. Gas Cleaning

An important aspect of a gasification process is the gas cleaning. Gas cleaning in gasification is usually associated with high cost (Dry 2002). Gas cleaning in gasification processes is performed generally from two aspects: the treatment and conditioning of the product gas. The treatment is usually done to remove undesirable impurities, while the conditioning of the gas is done to get the right \( H_2 \) to CO ratio (Basu 2010 304).

3.1. Gas Treatment

For synthetic reactions, a high degree of gas purity in required compared to the syngas applications in the generation of power. The raw syngas from gasification processes can contain impurities such as solid particulates, inorganic and organic impurities (Boerrigter et al. 2004). Cyclones, fabric or other barrier filters, electrostatic filters and a solvent scrubber are usually used in the removal of particulates. Organic impurities such as tars are removed by scrubbing with an organic liquid, catalytic cracking or by high-temperature cracking. The inorganic impurities are removed in the sequence, in order to avoid the formation of undesirable components from one particular removal process to another (Basu 2010 304).

3.1.1. Particulates

Particulate impurities in the raw syngas consist of unconverted char and ash. Cyclones are the most widely used devices for the collection of particles. They can be manufactured from carbon steel and are designed to operate at the typical operating temperature and pressure of the gasifiers (NREL 2006). Cyclones operate by using centrifugal forces to separates bulk of particulates (NREL 2006; De Nevers 2000 257-258). Further to that, a barrier filter can also be used to separate particulates. In the barrier filters (Fig. 13), particulates are captured as they pass through the filter medium, where they accumulate on the filter surfaces to form a cake and then are removed by a blowback flow (NREL 2006).
Barrier filters are broadly categorized into high-temperature and low temperature filters. The high-temperature filters are made up of ceramic and metal filters. The ceramic filters are used to remove particulates at elevated temperatures (1800°F=982°C), while the metallic filters are used to remove particulates at high temperatures (650-914°F=343-490°C). (NREL 2006) Furthermore, electrostatic precipitators (ESPs) can also be used to remove particles. The ESPs use electrostatic forces to drive the particles to a wall where they are collected. The ESPs are effective for the separation of relatively small particles. Additionally, wet scrubbers are also used to absorb the particulates in a liquid drop after contraction thereby making the particulates easy to be collected. (De Nevers 2000 266 & 298)

3.1.2. Inorganic Impurities

Depending on the feedstock, different inorganic impurities like sulfur compounds (H$_2$S, COS, CS$_2$) and nitrogen compounds (NH$_3$, HCN) are formed during the gasification process. The sulfur-based compounds in a syngas can lead to sulfur emission in power plants and catalysts poisoning in syngas syntheses. These compounds are undesirable and as such, they are often required to be reduced to a bearable level. The concentration of sulfur compounds in the syngas for applications in power generation and in syngas synthesis should be >300 ppm and >1 respectively (NREL 2006). However, H$_2$S is usually removed by absorption or through Claus process, while water washing is usually employed for NH$_3$ and halides removal (NREL 2006; Boerrigter et al. 2004). Other compounds such as COS and HCN are difficult to remove by these processes, however, they are captured in a guard bed. On the other hand, where they are present in higher loads, it is more feasible to install a hydrolysis step that could aid their conversion into H$_2$S and NH$_3$. In general, the inorganic impurities can be removed from
the raw hot syngas by first cooling with water. (Boerrigter et al. 2004). Figure 14 depicts the most widely used cleaning process of the inorganic impurities present in the raw syngas.

![Syngas cleaning diagram](image)

**Figure 14.** Syngas cleaning based on commercially available technologies (Adapted from Boerrigter et al. 2004).

### 3.1.3. Organic Impurities

Common organic impurities in a gasification process are methane, aromatics, carbon dioxide and tars. With the exception of tars, most of these impurities are completely destroyed especially in high temperature gasification. The high cost associated with tar cleanup is generally one of the major limitations of biomass-based distributed power generation (Basu 2010 98). Tars are thick, black and highly viscous liquid that are associated with a gasification process. Unlike coal tar, biomass tar has little or no commercial value and it is by far the greatest nuisance associated with a biomass gasification process (Basu 2010 103). Tar is formed generally with high amounts when
updraft gasifiers are employed, while low tar formation is observed with downdraft gasifiers (Devi et al. 2006).

In general, the raw hot syngas has to be cooled before cleaning the syngas. When it is cooled below the dew point of tar (700-750°F=371-399˚C), the tar may be deposited on the downstream equipment and piping thereby causing serious operational problems (NREL 2006). Tar condensation could also lead to the formation of tar aerosols that are difficult to remove from syngas (Devi et al. 2006). So where possible, tar has to be removed completely. However, in a gasification process whose product gas is to be used for instance in engines or turbines the removal of tar is envisaged on its allowable concentration in the engines. Table 4 below summarizes the tar tolerance limit for gas engines and turbines.

**Table 4.** Tar tolerance limits of different types of gas engines and gas turbines (Devi et al. 2006)

<table>
<thead>
<tr>
<th>Application</th>
<th>Allowable tar concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC Engine</td>
<td>&lt;10 mg/m³</td>
</tr>
<tr>
<td></td>
<td>Up to 30 mg/m³</td>
</tr>
<tr>
<td></td>
<td>&lt;100 mg/m³</td>
</tr>
<tr>
<td></td>
<td>&lt;100 mg/m³</td>
</tr>
<tr>
<td>Gas Turbine</td>
<td>0.05-0.5 ppm</td>
</tr>
<tr>
<td></td>
<td>0.5 mg/m³</td>
</tr>
</tbody>
</table>

The two methods for tar removal are in-situ or primary tar reduction and the post-gasification or secondary reduction (Fig. 15).
In the primary reduction, the formation of tar is controlled inside the gasifier while in the secondary method tar is removed at the downstream. Unlike in the secondary method, tar removal in the primary method influences the product gas. Tar reduction in in-situ method can be achieved by modification of the operating conditions inside the gasifier, use of catalysts or alternative bed materials as well as by the modification of the gasifier design. (Basu 2010 103-104; Devi et al. 2006)

However, in both methods tar is removed by either a physical or chemical process (Devi et al. 2006; NREL 2006). The physical processes employ cyclones, electrostatic precipitators, scrubbers, and barrier filters to separate tar. The chemical process on the other hand, can be done by thermal cracking, catalytic cracking or by the use of a high voltage plasma reactor (Devi et al. 2006). The catalytic tar cracking utilizes a catalyst to reform the tar in the reactor bed. In this method, the tar is converted into useful gases, and at the same time impurities such as light hydrocarbons, benzene and ammonia can also be removed (NREL 2006). However, to achieve appreciable degree of product gas purity by catalytic tar cracking, the use of a complex catalytic process is required (Narváez et al. 1996). Dolomite, nickel, alkali, olivine and char have found applications as catalytic and in-bed additive materials in tar removal (Basu 2010 107). Thermal cracking on the other hand, rely on the high temperature for the destruction of tar. However, the major drawbacks with thermal cracking are the loss of efficiency and the possible formation of soot in the process (Neeft et al. 1999).

### 3.2. Gas Conditioning

The syngas conditioning is essential in order to get the right \( \text{H}_2/\text{CO} \) ratio for the intended use of the syngas. The conditioning is mostly performed with the water-gas shift reaction and the separation of \( \text{CO}_2 \) from the syngas.

#### 3.2.1. Water-Gas Shift Reaction

The water-gas shift (WGS) reaction for the adjustment of \( \text{H}_2/\text{CO} \) ratio is required especially in the synthesis of fuels as well as in the production of pure hydrogen for applications in the fuel cells (Fu et al. 2003). In the applications of syngas for the fuel
syntheses, the H₂/CO ratio adjustment is beneficial for the catalysts that convert the syngas into liquid hydrocarbons. The WGS reaction (Eq. 14) is an exothermic reaction ($\Delta H_r = -41.1$ kJ/mol) that converts excess carbon monoxide into hydrogen (Basu 2010 304; Schulz et al. 2013).

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (14)$$

In general, the WGS reaction can be carried out either at the high temperatures or at low temperature. At high temperatures, catalysts based on iron and chromium oxides are used to catalyze the reaction. At low temperature the reaction can be catalyzed by catalysts based on copper, aluminum and zinc oxides. (Basu 2010 304) However, in recent times, interest has been shifted to a catalyst-membrane system that incorporates the WGS reaction and H₂ separation via a hydrogen selective membrane (Mendes et al. 2010). The aim of this process is to produce ultra-pure hydrogen for application in the fuel cells.

### 3.2.2. CO₂ Removal

CO₂ is one of the major by-products in a gasification process. The removal of CO₂ is desirable in order to reduce the CO₂ emissions or to meet the downstream process requirements. The basic factor in determining the technique for the removal of CO₂ from a gas stream is the partial pressure of the gas. At the present, absorption processes are the most developed techniques in the separation of CO₂ in the industries. Other techniques that are recently gaining interest are adsorption, membrane separation, cryogenics fractionation, hydrate based separation, chemical-looping combustion and enzyme based separation. The CO₂ separation techniques are investigated next more in-depth.
4. CO₂ Separation Techniques

The removal of CO₂ from a gas mixture represents a great challenge to power plants and other members of the CO₂ emitting industries. CO₂ capture techniques can be used for example in natural gas cleaning and in the production of hydrogen, ammonia and other industrial chemicals. The captured CO₂ is sequestered underground or in the ocean. Recently, the possibility to use the captured CO₂ as a raw material for the production of useful chemicals in different industries has been investigated. The decisive parameter in the selection of a carbon dioxide removal technique from a product gas is the partial pressure of CO₂ in the gas stream.

The overall need for gas purification is, however, dependent on the downstream requirements for the utilization of the important gas components. Furthermore, the existing regulations on greenhouse gases emissions have prompted a search for a capture and separation technology that could limit the release of CO₂ to a bearable level and, while maintaining the production costs at a relatively low level in the power plants and other related industries. There are four basic options for the capture of CO₂ in industries. These options are CO₂ capture from an industrial process stream, pre-combustion capture, post-combustion capture and oxy-fuel capture.

Generally, CO₂ is stored only if there are clear incentives or provisions for its storage. In pre-combustion capture, the fuel reacts with the air or steam to yield syngas via partial oxidation, gasification or reforming reactions. CO in the syngas undergoes further reaction with steam in a catalytic reactor to yield more hydrogen and CO₂. The formed hydrogen is combusted in gas engines and CO₂ is separated.

The post-combustion capture is performed with a downstream process where the separation of CO₂ is carried out after the combustion of the product gas. In this option, the flue gases are passed through equipment, capable of separating most of CO₂ for storage and venting the remaining flue gas into the atmosphere. (IPCC 2005 3, 108-109) However, the post-combustion capture has some challenges in the separation of CO₂. These challenges include the design challenges presented by the higher temperature of the flue gases, the need for a powerful chemical solvent in the separation of low concentration CO₂, and the higher energy penalty in the regeneration of the solvent (Mondal et al. 2012).
Oxy-fuel on the other hand, is a modified version of the post-combustion capture, which yields a flue gas comprised mainly of CO$_2$ and H$_2$O. This is enabled by using in combustion pure oxygen instead of air (Mondal et al. 2012; IPCC 2005 109). In this situation, the CO$_2$ can be purified at low cost, and the water vapor (H$_2$O) in the flue gas is removed by condensation (Mondal et al. 2012). However, in any of these options, there are a number of techniques that can be used in the removal of CO$_2$ from a gas stream. Some of these techniques mentioned below in Fig. 16 have already reached a development stage, but others require further improvements both in terms of technical capabilities and cost reduction.

**Figure 16. Technologies for CO$_2$ separation.**

### 4.1. Absorption

Absorption is based on the solubility differences of different gas components in a liquid solvent. Absorption processes can be further divided based on the solvent type into physical and chemical. The usage of a physical solvent is more advantageous when the concentration of CO$_2$ in the feed gas is high (Burr and Lyddon 2008). Some of the physical solvents that could be used for the gas purification of CO$_2$ are selexol, rectisol, purisol and flour processes. Selexol and rectisol are the most commonly used physical solvents especially in the IGCC processes (Korens et al. 2002). In a chemical solvent process, amine solution, aqua ammonia and dual-alkali are typically used.
However, the amine is widely used due to its mature technology e.g. by the natural gas industry (Yang et al. 2008). Furthermore, hybrid absorption that combines the advantages of the absorption efficiency of a chemical solvent and low energy regeneration potential of a physical solvent for gas separation is often used. Recently, ionic liquids (ILs) have also gained interest.

4.1.1. Selexol

Selexol solvent is a dimethyl ether of polyethylene glycol (DEPG) with the chemical formula \( \text{CH}_3(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3 \) where \( n \) is between 2 and 9. The solvent is chemically and thermally stable, with low toxicity and is non-corrosive (Burr and Lyddon 2008). The DEPG has low vapor pressure, hence losses due to vaporization is low (Yu et al. 2012). Additionally, the selexol process operates at a low temperature, but at high pressure. Hence, the solvent can be easily regenerated by reduced pressure or stripping (Olajire 2010). The solubility of CO\(_2\) in the solvent is relatively high compared to the ones of CO and H\(_2\) (see Table 5).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.5</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>2.2</td>
</tr>
<tr>
<td>Methane</td>
<td>5</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>75</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>675</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>7000</td>
</tr>
</tbody>
</table>

Table 5. Relative solubility of different gases in Selexol solvent (Kubek et al. 2000).

However, one major drawback of the selexol process is hydrocarbon losses due to the high affinity of the solvent to heavy hydrocarbons (Olajire 2010). Additionally, quite often, the temperature of the product gas has to be reduced in order to increase the solubility of CO\(_2\), as such DEPG could reduce mass transfer rates due to its high viscosity (Burr and Lyddon 2008). On top of that, due to its high selectivity for sulfur compounds present in a feed gas, the process is not suitable for deep CO\(_2\) removal (Kubek et al. 2000).

4.1.2. Rectisol

Rectisol process involves the use of an organic solvent composed mainly of methanol, which is widely used in CO\(_2\) and H\(_2\)S removal from gas stream. Methanol is a light, colorless and volatile compound. Further to that, methanol does not foam, it is miscible
with water, and has high thermal and chemical stability and is also non-corrosive (Hochgesand 1970). The solubility of CO\(_2\) in methanol is relatively high compared to other gas constituents (see Table 6).

**Table 6.** Relative solubility of different gas components in methanol at -40°C (Rousseau *et al.* 1981).

<table>
<thead>
<tr>
<th>Component</th>
<th>Relative solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>5.2</td>
</tr>
<tr>
<td>Methane</td>
<td>11.7</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>434.8</td>
</tr>
<tr>
<td>Carbonyl sulfide</td>
<td>1565.2</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>2521.7</td>
</tr>
</tbody>
</table>

However, the process is complex in nature, and operates at low temperature due to the high vapor pressure of the solvent (Burr and Lyddon 2008). Rectisol process can be designed in a single-stage or a two-stage configuration. The single-stage configuration uses a single absorber column, while the two-stage process uses two absorber columns and two solvent regeneration systems (Sun and Smith 2013). In both stages, a gas stream is cooled down to a low temperature before it is fed to the bottom of the absorber under high pressure. However, due to the high solubility of the sulfur compounds present in the feed gas, the absorber is designed into two sections. CO\(_2\) is removed at the upper section and sulfur compounds are removed at the lower part of the absorber. The purified gas is usually collected at the top of the absorber (Hochgesand 1970; Sun and Smith 2013).

The use of rectisol for gas cleaning offers more advantages than using selexol. For instance, hydrocarbon losses in the rectisol process are low compared to the ones in selexol process. Additionally, besides the removal of CO\(_2\) and sulfur compounds, other impurities such as HCN and NH\(_4\) can also be removed simultaneously (Weiss 1988). However, due to complexity of the process, the solvent has to be refrigerated, which could lead to high capital and operating costs. (Burr and Lyddon 2008)

**4.1.3. Purisol**

Purisol solvent is N-Methyl-2-Pyrrolidone (NMP). Similarly as selexol, it has high chemical and thermal stabilities, is non-corrosive, has a low vapor pressure hence, minimal losses are formed due to vaporization. Purisol process can be operated at the ambient temperature, can also serve as dehydrating agent and is easily recovered by
backwashing with water. In the process, the high pressure gas absorption of CO\textsubscript{2} takes place in the absorber. The purified gas components are released from the gas stream and the solvent is regenerated at the middle of the absorber. (Hochgesand 1970). Purisol process is also characterized with low energy consumption (Yu et al. 2012). However, the main challenge with this kind of a process is the compression of CO\textsubscript{2} in a raw gas (Hochgesand 1970).

4.1.4. Flour process

This process uses propylene carbonate (PC) as cheap solvent. The process is suitable for CO\textsubscript{2} removal at moderate temperature and can be operated with low capital costs (Bucklin and Schendel 1985 42). The process is also suitable when the CO\textsubscript{2} partial pressure is higher than 4 bar (Yu et al. 2012). High solubility of CO\textsubscript{2} in the solvent, culminating with bulk CO\textsubscript{2} removal, minimum hydrocarbon losses and series of flash tanks for solvent regeneration, as well as low solvent losses has made PC an attractive solvent for gas purification (Bucklin and Schendel 1985 42). Olajire (2010) summarized the advantages of the flour process as follows:

- No additional heat is required for solvent regeneration
- The process does not require makeup water
- Dry gas is collected as output product
- The process is applicable in winter regions (PC freezes at -49°C)
- High CO\textsubscript{2} solubility.

However, separation of H\textsubscript{2}S present in a gas stream requires usage of a very high temperature in this process (Olajire 2010). In addition to that, an acid gas that dissolves in PC could be easily hydrolyzed to [H\textsuperscript{+}] by water. This could lead to the corrosion of equipment and pipes. (Hua et al. 1999)

4.1.5. Amines

The use of amine-based solvents for gas purification processes is a matured technology. Amines are compounds derived from ammonia. Typically monoethanolamine (MEA), diethanolamine (DEA) or triethanolamine (TEA), are used as the solvents. Among these amines, MEA is the most widely used for CO\textsubscript{2} separation in industries. MEA possesses high ability to absorb CO\textsubscript{2} at low pressure, and is relatively cheap. The mechanism is based on the reaction between amine and CO\textsubscript{2} in an absorber until equilibrium is
reached. The reaction yields MEA carbamate. The CO₂-rich carbamate MEA is reheated with steam in the stripper column to release the CO₂ and the MEA is recycled back to the absorber (McCann et al. 2008). The gas stream and the solvent are usually fed at the bottom and top of the absorber respectively. The reaction between the feed gas and the solvent in the absorber result in the absorption of CO₂ at a suitable CO₂/MEA ratio. This reaction mechanism is the same as with DEA, but the TEA reaction could facilitate the CO₂ hydrolysis reaction to form bicarbonate, due to the absence of hydrogen atom to bond to the nitrogen atom. (Booth 2005 16-17) Further to that, the difference in the heat of reaction in the formation of bicarbonate is lower than that of carbamate as such TEAs are often blended with primary or secondary amines (Vaidya and Kenig 2007).

![Figure 17](image_url)

**Figure 17.** Amine-based CO₂ absorption phenomena (Adapted from McCann et al. 2008).

Although CO₂ absorption on an amine is a developed technology, however, the process has some drawbacks. The major drawbacks are the large equipment size requirement, energy penalty especially in the regeneration of the solvent, low carbon dioxide loading capacity (0.5 mole CO₂/mol amine), corrosion of equipment by O₂ and degradation of the solvent by SOₓ, HCl, NO₂, and HF present in the feed gas stream (Idem et al. 2006; Resnik et al. 2004; Yeh et al. 2005). Regeneration of amine-based solvents could raise the operating cost of a carbon capture plant to about 70% of the total costs (Idem et al. 2006). Recently, mixed amine solvents that could retain the reactivity of the solvent, reduced circulation rates and substantial energy saving are investigated (Idem et al. 2006). In addition to that, an aqueous piperazine (PZ) that acts as a promoter for enhanced kinetics of amine systems can also be used. PZ has high CO₂ absorption rate,
with little or no thermal degradation of the solvent and possesses higher CO₂ loading capacity compared to the usage of an amine without a promoter. (Bishnoi and Rochelle 2002; Xu et al. 1998)

4.1.6. Ammonia

The use of aqueous ammonia was reported to offset the cons of MEA-based absorption of CO₂ due to its high loading capacity, non-corrosive, non-degradation of the solvents and low energy penalty in the regeneration of the solvent. The process employs the preheating of a gas, which reacts with aqueous ammonia in a wet scrubber. The regeneration of the solvent is done by the addition of heat, which could aid the decomposition of ammonium bicarbonate and ammonium carbonate formed in the process. The regeneration step in aqueous ammonia process could reduce the energy consumption to about 75% of the costs compared to the MEA process. The by-products of this process are mainly ammonium nitrate and ammonium sulfate. These compounds are useful fertilizers for agricultural purposes. (Yeh et al. 2005) The process chemistry is represented in Eqs. (15-18).

\[
\begin{align*}
\text{CO}_2 (g) + \text{H}_2 \text{O (l)} & \leftrightarrow \text{CO}_2 \cdot \text{H}_2 \text{O (l)} \quad (15) \\
\text{CO}_2 \cdot \text{H}_2 \text{O (l)} + \text{OH}^- & \leftrightarrow \text{HCO}_3^- + \text{H}_2 \text{O} \quad (16) \\
\text{HCO}_3^- + \text{OH}^- & \leftrightarrow \text{CO}_3^{2-} + \text{H}_2 \text{O} \quad (17) \\
\text{CO}_3^{2-} + \text{H}^+ & \leftrightarrow \text{HCO}_3^- \quad (18)
\end{align*}
\]

Generally speaking, an increase in temperature and a high pH will result in effective absorption of CO₂. Under these favorable conditions, the absorbed CO₂ will dissociate to form bicarbonate and carbonate ions. High pH favored desorption of the aqueous ammonia from the solution (Eqs. 19-20) hence, an increase in the absorption efficiency. However, under certain concentration, the ammonia is lost to ammonia gas which could result in low absorbent efficiency. Furthermore, the absorption of CO₂ with aqueous ammonia could produce salt crystals (Eqs. 21-25) that could disrupt the process through pipe blockage or scales of the walls. (Yeh et al. 2005)
\[
\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 \cdot \text{H}_2\text{O} \quad (19)
\]
\[
\text{NH}_3 \cdot \text{H}_2\text{O} \leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \quad (20)
\]
\[
\text{HCO}_3^- + \text{NH}_4^+ \leftrightarrow \text{NH}_4\text{HCO}_3 \text{ (l)} \quad (21)
\]
\[
\text{NH}_4\text{HCO}_3 \text{ (l)} \leftrightarrow \text{NH}_4\text{HCO}_3 \text{ (s)} \quad (22)
\]
\[
\text{CO}_3^- + 2\text{NH}_4^+ \leftrightarrow (\text{NH}_4)_2\text{CO}_3 \text{ (l)} \quad (23)
\]
\[
(\text{NH}_4)_2\text{CO}_3 \text{ (l)} \leftrightarrow (\text{NH}_4)_2\text{CO}_3 \text{ (s)} \quad (24)
\]
\[
(\text{NH}_4)_2\text{CO}_3 \text{ (s)} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{NH}_4\text{CO}_3 \text{ (s)} \quad (25)
\]

### 4.1.7. Dual Alkali

An alkali can also be used to capture \(\text{CO}_2\) from a gas stream. The process involves the transformation of \(\text{CO}_2\) into sodium carbonate in the presence of ammonia. The ammonia acts as a catalyst, which can be recovered via a reaction with chloride and lime as secondary alkali (Eqs. 26-27).

\[
\text{CO}_2 + \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 \downarrow + \text{NH}_4\text{Cl} \quad (26)
\]
\[
2\text{NH}_4 + \text{Ca(OH)}_2 \rightarrow 2\text{NH}_3 + \text{CaCl}_2 + \text{H}_2\text{O} \quad (27)
\]

However the secondary alkali (lime) usage in the recovery of ammonia could result in the consumption of lime, formation of \(\text{CO}_2\) (\(\text{CO}_2\) capture and release is in the ratio of 2:1) and energy penalty in the calcination process. Equations 28-29 below represent the process chemistry.

\[
\text{CaCO}_3 \rightarrow \text{CaCO}_3 + \text{CO}_2 \quad (28)
\]
\[
2\text{NaCl} + 2\text{CO}_2 + \text{CaO} + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 + \text{CaCl}_2 \quad (29)
\]

However, the use of a methylaminoethanol (MAE) as replacement of the primary alkali could lead to the formation of bicarbonate precipitation and improved absorption efficiency. (Huang et al. 2001)
4.1.8. Hybrid Absorption Process

Sulfinol and amisol processes are physico-chemical absorption processes that combine the advantages of the absorption efficiency of a chemical solvent and the low energy regeneration potential of a physical solvent for gas separation. Basically, the physical solvent removes most of the impurities, while the final products are purified by the chemical solvent (Marklund and Öhrman 2011). The process could enhance the rate of acid gas removal from gas stream, with absorption and regeneration sections working simultaneously.

4.1.9. Ionic Liquids

Ionic liquids (ILs) can also be used to absorb CO₂ from a gas stream. ILs are gaining great interest due to their multiple beneficial properties. ILs are organic salts with an extremely low vapor pressure. In addition, they are non-flammable, and have a low toxicity level (Zhao 2006). The solubility of CO₂ in ionic liquids is relatively high compared to other components, for example H₂, CH₄, N₂, CO and O₂. Further to that, the energy penalty in the regeneration of ILs is quite low compared to conventional absorption processes. ILs are also considered to be efficient and environmentally benign solvents (Fukaya et al. 2008). At room temperature, high CO₂ sorption capacities and rapid sorption kinetics can be achieved using ILs (Lee et al. 2012). Therefore, with its beneficial properties and separation performance, in the future, ILs could be one of the competitive candidates in the separation of CO₂ from a gas stream.

4.2. Adsorption

Adsorption is a gas separation technology where certain gas components adsorb preferentially on an adsorbent. The technique is currently used e.g. by the natural gas industry to remove water and other impurities (Tagliabue et al. 2009), in the removal of CO₂ and other gases in a post-combustion process (Ebner and Ritter 2009), in the purification of methane in coal mining (Tonkovich 2004) and in biogas cleaning (Alonso-Vicario et al. 2010). Similarly, as in the absorption processes, the adsorption process has a sorptive stage and a regenerative stage. Adsorption can be either physical or chemical in nature. The process phenomenon is based on the creation of a suitable surface area on a material to which the gas components can bind at a low temperature (Marklund and Öhrman 2011; Watson et al. 2009). The regeneration is based on the utilization of differences in adsorption loadings at various temperatures (thermal-swing
adsorption, TSA) and at different pressures (pressure-swing adsorption, PSA) (Watson et al. 2009). In PSA, the bed can be regenerated by reducing the pressure, but for TSA, regeneration is often done by raising the temperature (Yu et al. 2012). Examples of adsorbents are molecular sieves, activated carbon, metal-organic frameworks (MOFs), and lithium compounds.

4.2.1. Molecular Sieve

Molecular sieves are materials with small holes with uniform sizes. The materials can be divided into microporous, mesoporous or macroporous depending on their pore sizes. The microporous molecular sieves operate in the presence of a specific porous network containing pore mouths of molecular dimensions, and with a relatively high micropore volume. Molecular sieves differentiate gas molecules based on their sizes, shapes or on the difference in adsorption equilibrium or adsorption rate (Wahby et al. 2012). Due to their uniform pore size distributions and the pore size being only several ångstrom diameters, molecular sieve can separate gases with high selective adsorption efficiency (Yu et al. 2012). The adsorption capacity of CO$_2$ on molecular sieve depends on the total pore volume, surface area, the volume of the narrow micropores and the adsorption density (Wahby et al. 2012).

4.2.2. Activated Carbon

Activated carbon can be produced from hardwoods, coconut shells, fruit stones, coal and petroleum pitch whose porosity is enclosed by carbon atoms (Harry and Francisco 2006). The pore size nature of activated carbon has made it as an attractive material for CO$_2$ separation from a gas stream. The adsorption capacity of activated carbon is dependent upon the temperature and the CO$_2$ partial pressure in a gas stream. At high partial pressure, CO$_2$ adsorption is high, but low at high temperature (García et al. 2011). Conversely, at low CO$_2$ partial pressure, the adsorption capacity of activated carbon is low due to the presence of water vapor (Lopes et al. 2009). In general, activated carbons are also characterized by low selectivity to CO$_2$ (Li et al. 2011). Maroto-Valer et al. (2005) has investigated the improvement in the modification of the CO$_2$ adsorption capacity of the activated carbon by activated and impregnated anthracites. However, in their study, they found that the CO$_2$ capture has no linear relationship with the surface area. A profound modification of the surface material for effective adsorption was the use of a heteroatom such as nitrogen. The heteroatom
behaves in the form of acidic, basics or neutral organic functional groups (Arenillas et al. 2005). However, the introduction of the functionalities should be carefully done to avoid altering the textural properties of the parent carbon (Pevida et al. 2008).

4.2.3. Metal-Organic Frameworks

Metal-Organic Frameworks (MOFs) are crystalline porous materials that are coordinated by metal-containing nodes to organic bridging ligands. The structure of MOFs is robust enough to allow the removal of guest species. (Li et al. 2011) The crystallinity of MOFs allows the precise structural characterization by a diffraction method, which facilitates their rational design and the formulation of structure–function relationships (Li et al. 2009). Additionally, in the post-synthesis of MOFs, the pore properties of the materials can be tuned, which differs from the properties of the conventional porous materials (Wang and Cohen 2009; Li et al. 2009). In general, the attractiveness of MOFs in gas separation is based on their thermal stability, large surface areas, adjustable pore sizes and controllable properties (Li et al. 2009; Yu et al. 2012). Because of these properties, the CO\textsubscript{2} adsorption and uptake by a MOF is higher compared with other porous materials (Li et al. 2011). MOFs can be classified into rigid and flexible. The rigid MOFs possess stable and robust porous frameworks with permanent porosity. The flexible MOFs on the other hand, possess dynamic, “soft” frameworks that can respond to an external stimulus, such as pressure, temperature, and guest molecules. (Li et al. 2011)

4.2.4. Chemical Adsorption with Lithium Compounds

Lithium compounds can be used in gas preparation to chemically adsorb different components. The most widely used lithium compound for CO\textsubscript{2} removal from a gas stream is lithium zirconate. The adsorption process is reversible and is generally performed at the temperature range of 450-590\degree C. The reversible adsorption reaction is the following (Ida et al. 2004):

\[
\text{LiZrO}_3 \text{ (s)} + \text{CO}_2 \text{ (g)} \leftrightarrow \text{LiCO}_3 \text{(s)} + \text{ZrO}_2 \text{(s)}
\] (30)
Lithium compounds-based CO₂ separation promotes high CO₂ adsorption capacity, but could be affected by the aggregate size of the LiCO₃ (Fauth et al. 2005). Therefore, the Improvement of the process efficiency can be performed through the decrease in the particle size (Ida et al. 2004).

4.3. Cryogenic Fractionation

CO₂ can also be removed from a gas stream by cooling and condensation in the applications where the concentration of CO₂ in a gas stream is high. This process is known as cryogenic fractionation. In post-combustion capture the gas stream is cooled to a very low temperature for CO₂ to be captured in liquid form and subsequently separated. The greatest benefit for this capture and separation technique is the possibility to produce liquid CO₂, which can be transported by ship. In addition to this, pollutants such as Hg, SOₓ, NO₂, and HCl can be removed with a high efficiency (Burt et al. 2009). However, the main challenges with this technology are the high-energy consumption, high costs and the formation of frosted CO₂ (Meisen and Shuai 1997; Tuinier et al. 2010).

4.4. Membrane Separation

In membrane separation, the separation is based on the relative permeation rates of each component. The component with the fastest permeation rate concentrates on the permeate side. Due to the simplicity of a membrane process, higher energy efficiency, and environmental compatibility (Xiao et al. 2009; Zhang et al. 2013), membrane separation is considered to be one of the future techniques in CO₂ separation. Gas separation by membranes offers high selectivity by differentiating gases according to their sizes, shape and chemical properties (IPCC 2005 10). In general, for a membrane to be competitive in CO₂ separation it should have high CO₂ permeability and selectivity, it should be thermally and chemically robust, resistant to plasticization and aging, and it should be cost effective, as well as able to be manufactured cheaply into different membrane modules (Powell and Qiao 2006). Membranes for gas separation are broadly classified into polymeric and inorganic membranes.

4.4.1. Polymeric Membranes

In the polymeric membrane separations, CO₂ can be separated at a low cost, with a high separation performance, and overall mechanical stability (Scholes et al. 2009).
Polymeric membranes are made up of glassy and rubbery types. The glassy membranes are rigid and glassy-like. The membranes are highly selective, but have low permeability. The rubbery membranes, on the other hand, are flexible and soft. Therefore, the membranes are characterized by high permeability but low selectivity. However, the transportation of a gas molecule in polymeric membranes is governed by the polymer properties and is also influenced by the solution-diffusion mechanism (NETL 2003 44-45). In this mechanism, a gas component is sorbed at the entering stage, dissolves on the polymer and then diffuses through the membrane and desorbs at the exit. Similarly, selectivity within the polymeric membranes is governed by the molecule sizes of the permeating components. The molecule sizes are normally determined by their kinetic diameters, whereas permeability is governed by gas solubility. Eq. (31) below represents the diffusivity coefficient and solubility of the transporting gas molecules in a polymeric membrane. (Zhang et al. 2013).

\[ \hat{P}_i = D_i \cdot S_i, \quad (31) \]

where \( \hat{P}_i \) is the permeability of a component \( i \) through the membrane, \( D_i \) and \( S_i \) are diffusivity and solubility of a component respectively. Similarly, the selectivity of component \( i \) with respect to component \( j \) is given by their permeability ratio as expressed in Eq. (32).

\[ \alpha_{ij} = \frac{\hat{P}_i}{\hat{P}_j} = \left( \frac{D_i}{D_j} \right) \left( \frac{S_i}{S_j} \right). \quad (32) \]

However, the main drawbacks with the use of polymeric membranes in gas separations are the competitive adsorption of condensable water with CO\(_2\), and plasticization of the membrane. The plasticization the membrane can turn a glassy polymer to a more rubbery state, which hinders both gas permeability and selectivity (Scholes et al. 2009). Another bottleneck is the efficiency losses in the polymeric membranes (Franz and Scherer 2010).
4.4.2. Inorganic Membranes

Inorganic membranes are porous or non-porous depending on their structures. The porous inorganic membranes consist of a porous thin top layer casted on a metal or ceramic that offers mechanical strength, but minimal mass transfer resistance. The non-porous inorganic membranes are made of up of thin layer of metal or solid electrolyte that is used in a high selective gas separation (Yang et al. 2008). Inorganic membranes are highly stable at high temperatures and can withstand harsh conditions compared to the polymeric membranes (Caro et al. 2000). Inorganic membranes can be made from alumina, carbon, glass, silicon carbide, titania, zeolite, or zirconia.

Generally, membranes are supported on different substrates, such as α-alumina, γ-alumina, zirconia, zeolite, or porous stainless steel (Yang et al. 2008). However, at low temperature alumina tends to undergo phase transition, but due to the mesoporous structure of alumina, its chemical and hydrothermal stabilities beyond 1000°C, α-alumina and γ-alumina have found application mainly as support materials (NETL 2003 13).

Carbon membranes on the other hand, are classified into supported and unsupported carbon membranes. Generally, the support is made of a porous material. Unsupported carbon membranes are brittle and mechanically unstable. Hence, problems may arise in the handling of unsupported carbon membranes. (NETL 2003 22) In general, carbon tends to exhibit substantial changes in pore size in an oxidizing environment (Centeno and Fuertes 2000). Other factors that can contribute to the limitations of the carbon membranes are the large thickness of the membranes (NETL 2003 22), high cost, lack of suitable precursor polymer, membrane preparation method and the carbonization process (Fuertes et al. 1999)

Silica is foreseen as an interesting material for gas separation, due to its exceptional thermal, chemical and structural stability in both oxidative and reductive atmospheres (Fuertes and Centeno 1998). Silica is a very versatile material for gas separation membranes because its structure can be tailored by changing the preparation method and conditions. However, diffusion in amorphous silica with very small pores is relatively slow, but this could be improved in the preparation of the silica membranes. The silica membrane can be prepared either by the sol-gel method, chemical vapor deposition or phase separation method. However, due to its controllability and
homogeneity, sol-gel method is often used in the membrane synthesis or pore modification (NETL 2003 33).

One significant developing field around, is research into using zeolite membranes for gas separation. The membranes are presumed to be attractive in gas separation due to the presence of molecular-sized cavities as well as their thermal stability, solvent resistance and shape selectivity (Caro et al. 2000). The electrical charge or polarity of the zeolites promotes the attraction or sorting of molecules. The ability of zeolite to selectively adsorb molecules by size and polarity is the key to their unusual efficiency for gas separation (NETL 2003 14). The rate of gas permeability through the zeolite membranes is determined by both molecular sizes relative to the zeolite pore, and the relative adsorption strengths (Poshusta et al. 2000; Keizer et al. 1998). The experimental part of this study focuses on the separation of CO\textsubscript{2}/N\textsubscript{2} mixture using MFI type zeolite membranes.

4.4.3. Mixed Matrix Membranes

The use of mixed matrix membranes (MMMs) for gas separations is aimed at offsetting the cons of selectivity and permeability of the polymeric membranes, and significantly higher cost and handling difficulty associated with inorganic membranes (NETL 2003 64-65). MMMs utilize the easier operation of polymer and separation performance of inorganic membranes. The design of MMMs is usually done by the addition of porous inorganic filters into polymer matrix (Chung et al. 2007). The most researched MMMs for gas separation are based on zeolites bounded with polymeric membrane. However, a good contact between the inorganic materials and the polymer interface is the major challenge associated with this separation technique. A bad interface could lead to a gas molecule to bypass the sieve resulting into a poor performance. (NETL 2003 65)

4.4.4. Hybrid Membrane

The hybrid membrane for gas separation is the modified version of inorganic membranes. The modification can be done through the introduction of organic affinity to a particular gas component on the surface of an inorganic membrane (NETL 2003 55). This may improve the separation performance by allowing large flux of CO\textsubscript{2} through the porous inorganic materials leading to high selectivity and permeability. High CO\textsubscript{2} affinity could result in high performance in respect to selectivity and
permeability. In contrast, too strong CO$_2$ affinity of the membrane could result in weaker surface diffusion (Takaba et al. 1996).

**4.4.5. Facilitated Transport Membrane (FTM)**

Facilitated transport membrane (FTM) is another emerging technology for gas separation that was patented by Hagg. FTM are gaining interests as a potential technique for gas separation due to higher selectivity and larger fluxes (Way and Noble 1992). The process is based on the reversible reaction between a carrier agent and a penetrating species. The penetrating species dissolves in the upstream part of the membrane to form a complex, which diffuses across the membrane. In the downstream side of the membrane, permeate is released, and the carrier agent is recovered and diffuses back on the side of the feed gas stream. (Hagg and Kim 2005) However, the development of FTMs for gas separation may be very complex, which often creates multidisciplinary challenges in chemistry, chemical engineering and material science. In general, for FTMs to be competitive with the conventional techniques in gas separation, a complex agent in FTM must be able to withstand degradation and poisoning as well as exhibit long term stability (Way and Noble 1992).

**4.5. Hydrate Based Separation**

The search for a suitable CO$_2$ separation process from a gas stream has triggered research into hydrate based separation techniques. The hydrates have the ability to storage large amount of gas (Li et al. 2010). In the hydrate separation process, a gas stream is exposed to water under a high pressure to form a hydrate. A gas stream containing CO$_2$ that forms a hydrate, the CO$_2$ partitions in the hydrate phase (Linga et al. 2007). Hydrate based CO$_2$ separation with a suitable promoter has the potential of reducing the operating pressure and promotes the kinetic rates (Kang et al. 2001). However, some of the main drawbacks with the hydrate based separation processes are high energy consumption, slow hydrate formation rate and low separation efficiency (Li et al. 2010).

**4.6. Chemical-Looping Combustion (CLC)**

Chemical-looping combustion (CLC) is one of the emerging technologies for the separation of gases. CLC integrates two reactors (air and fuel reactors) and oxygen is circulated between the reactors for oxidation process. In this process a gas mixture
mainly CO₂/H₂O is formed and the formation of NOₓ can be offset. During the oxidation process, a metal oxide (MeₓOᵧ) is reduced in the fuel reactor, where it is then transported to an air reactor (Fig. 18). CLC can be integrated into a refinery gas, natural gas or in a gasification process for the capture and separation of CO₂ (Morin and Corinne 2005).

Figure 18. Principle of chemical-looping combustion process (Adapted from Morin and Corinne 2005).

4.7. Enzyme Based Separation

Enzymes are also gaining interest as a potential technique for CO₂ separation. The process is based upon a reaction between CO₂ and a living organism (Mondal et al. 2012). The benefits of the enzymes include mild process conditions (energy savings, high yields, less harmful side reaction) and the renewability. One of the enzyme-based CO₂ capture techniques that is gaining attention, is the usage of carbon anhydrase (CA) enzyme in a hollow fiber contained liquid membrane. The concept behind this process is the use of an immobilized enzyme at the gas-liquid interface. This could lead to an increased mass transfer rate as well as efficient CO₂ capture from a gas stream (Figueroa et al. 2008). However, some technical challenges are attributed to this process. These challenges include membrane boundary layers, pore wetting, surface fouling (Boa and Trachtenberg 2006), loss of enzyme activity, long-term operation and scale-up (Figueroa et al. 2008). For a breakthrough in addressing these challenges, enzymes based separation could be one of the future alternative technologies for CO₂ separation from a gas stream.
Experimental Part

5. Description of Equipment and Materials

The aim of the experimental work is to separate CO₂ from the mixture of CO₂/N₂. To achieve this, a number of equipment and materials were used in the process. A detailed description of the equipment and materials used in this study are presented below.

5.1.1. Gas Chromatography

The use of gas chromatography to analyze gas composition in the laboratory is a common practice. The GC-TCD used in this study was procured from Agilent Technologies USA (Serial number-US1034074). It consists of a column that separates the analyzed components, and the inlet where the samples are injected to the column, a detector that sensors the samples, a wire, an oven that provides the required heat to the column and a data system. In this study, the GC-TCD was used to compare the thermal conductivity of gas flows between a carrier gas and a gas sample. The wires were heated and undergo changes in temperature, which influences the thermal conductivity of the gases. The change in thermal conductivity is measured as it is sensed as a change in electrical resistance. The carrier gas used in this study was helium.

Figure 19. Gas chromatography with thermal conductivity detector.
5.1.2. Experimental Equipment

The gas flow rates, temperature and pressure measurements, preparation of gas mixtures, and heating rates, were all monitored in an automation monitoring system under a LabView environment. The laboratory equipment is originally from Xytel Europe B.V., but has undergone a multitude of changes during the experimental work. The system is made up of series of valves, mass flow controllers, an installed flow meter, an electric furnace, a built-in monometer and a thermometer (Lange and Rehberg Bochum, Germany), and a membrane cell. The system is shown in Figure 20.

![Experimental equipment](image)

**Figure 20.** Experimental equipment.

5.1.3. Mass Flow Controllers

Mass flow controllers are devices used to control the flows of gaseous or liquid substances. They are designed and calibrated such that they can control the flow of the gases at a particular flow rate range. The mass flow controllers used in this study were Bronkhorst High-Tech B.V. types (Models F-201CV-20K-AAD-22-Z, F-201C-5K0-AAD-35-Z, F-231C-FA and F-231C-FA-33-V). They consist of a thermal flow sensor, a control valve, and a microprocessor. In this study, three mass flow controllers were in the feed side and one in the permeate side.
5.1.4. Gas-tight Syringe

Syringes are nowadays used to collect or dispense samples in the laboratories. The syringe used in this study was procured from Hamilton Co. in USA (Model S-1000). The syringe was gas-tight and it is made up of an acrylic barrel and a silicone fluid tubing. Additionally, the syringe has a maximum volume of 1000 ml. In this study, the feed, permeate and retentate samples were taken once on each experimental point and analyzed in the GC using the gas-tight syringe. The samples were taken after the experimental conditions (temperature, pressure and flow rates) has stabilized in the experimental equipment. Figure 21 depicts this equipment.

![Gas-tight syringe](image)

**Figure 21.** Gas-tight syringe.

5.1.5. Electric Furnace

Furnace is used to pre-heat the gas before its enter the membrane cell. The furnace used in this study has been acquired from Applied Tests System Inc. (Series 3210). It is made up of a stainless steel shell and a ceramic shell heater. Additionally, the furnace has heat equalizing liners, and an extensometer slots. Also in the furnace, there are thermocouples, an end cap, a viewport, a gas port, cast brass heating elements and a temperature control system.
5.1.6. Membranes

In this study, the separation of CO$_2$/N$_2$ mixture was done using two supported hydrophobic high silica MFI type zeolite membranes. The membranes are called herein as ZSM5-I and ZSM5-II membranes. The membranes and membrane cell are shown in Fig. 23a and 23b.

Figure 22. Electric furnace.

Figure 23. a) Zeolite membranes (ZSM5-I and ZSM5-II) and b) the membrane cell.
The preparation of the membranes is beyond the scope of this study. However, both membranes have an inner diameter of 6mm and a length of 10cm. They have also a porous graded $\alpha$-alumina layer as a support material. The support material has a diameter of 6mm that consists of 30 µm thick top layers with pore sizes of 100 nm and a thick layer with 3 µm pore size. The exact Si/Al ratio of the membrane is not available. The membranes were sealed with O-rings and placed in a stainless steel and surrounded by heating mantle (Fig. 24).

![Diagram of membrane setup](image)

**Figure 24.** Membrane in stainless cell surrounded with heating mantle

### 5.2. Drying

Prior to the separation experiments, the membrane was dried to desorb the adsorbed components, the main component being water. In the process, the membrane was placed in the stainless steel cell. The cell was wrapped with an insulator, and then covered with an aluminum foil and an aluminum tape. The membrane was dried at the rate of 1°C min$^{-1}$ with the aid of a heating mantle. The heating was done from room temperature to 200°C for about 4.25 hours in a 0.1 l min$^{-1}$ nitrogen flow (99.999%, AGA). The temperature was steady for 8 hours before it was cooled down to the room temperature, at the cooling rate of 1°C min$^{-1}$ for another 4.25 hours. The drying was done overnight before the start-up of the separation experiments. Figure 25 below depicts the drying of the membrane.
5.3. Calibration of Gas Chromatography Analysis

The gas chromatography calibration routines were also carried out prior to the separation experiments. The calibration was done with the CO\textsubscript{2}/N\textsubscript{2} mixtures (1:1, 2:3, 3:2, 4:1, 1:4, and 9:1), 100% CO\textsubscript{2} and 100% N\textsubscript{2}. In the preparation of these mixtures, the flow of a pure gas component in a cylinder was controlled by mass flow controller. The pressure was set to 3.5 bar in all the calibration routines. All these were monitored in the LabView environment. However, the flow rate, pressure and temperature were measured with drum-type gasmeter (Ritter Apparatebau GmbH & Co. Serial No: E6BZ-WZ6C), built-in monometer and thermometer respectively. These measurements and readings were used to calculate the total flow rate and the mole fractions of the gases through the usage of the ideal gas equation. However, the CO\textsubscript{2}/N\textsubscript{2} mixtures were all prepared based on these calculations, after which the same procedure as with the pure component was also repeated with the mixtures. The samples were then collected with the gas tight syringe and injected in the gas chromatography. The samples were injected in the GC column in series of 3. The duration of the analysis was 3 minutes. The samples were analyzed by the gas chromatograph. The temperature for the injector, column and detector were set to 150 °C. The average feed compositions of each of the samples from the GC analysis were taken. The calibration curves i.e. the relation between peak area and sample compositions of the gases were determined (see section 6.1).
5.4. Pure Components Permeation Tests

The pure component permeation tests were also carried out with the experimental equipment. In the tests, the flows of each of the pure gas components were set at 2 l/min and monitored in the automatic monitoring system in the Labview. The flow of the pure gas components were also controlled by the mass flow controllers. The tests for each of the pure component were done both at low (300K) and high (373K) temperatures. The membrane was placed in the stainless steel that was wrapped with insulator and then covered with an aluminum foil and an aluminum tape. In the high temperature tests, the feed gas was pre-heated with the electric furnace. Additionally, all the tests were done at 3 different pressures (6, 3 and 2 bar) and the constant permeate pressure of 1 bar. After the pressures had stabilized, and the desired temperature was attained, the permeate flow rates were measured from the installed flow meter in the system. The temperature and pressure relative to the atmospheric pressure readings were also taken from the installed thermometer and monometer respectively. These measurements and readings were converted to NTP conditions through the usage the ideal gas equation. Hence, the permeate flow rates at NTP conditions were obtained. Relative permeabilities and permeation fluxes of the single pure gas components, at these pressures were also determined from the calculated permeate flow rates.

5.5. Separation Experiments

Table 7 below illustrates the selected feed compositions of CO₂/N₂ mixtures, as well as the compositions of the product gas from the HighBio biomass gasification project. The HighBio product gas compositions were based on the previous study on biomass gasification conducted by the partners in this project. The procedure for the preparation of the mixtures were similar to the gas chromatography routines (see section 5.3), except that the feed pressure was set to 6 bar in all the separation experiments. The flow of the gases from the cylinders was also controlled similarly as it was done in the previous sections (sections 5.3 and 5.4).
Table 7. The selected gas compositions and the HighBio product gas compositions.

<table>
<thead>
<tr>
<th>Samples of the selected gas compositions</th>
<th>CO₂:N₂</th>
<th>1:1</th>
<th>4:1</th>
<th>9:1</th>
<th>1:9</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂:N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HighBio product gas compositions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂:N₂</td>
<td></td>
<td>2.3:7.8</td>
<td></td>
<td>2.8:7.2</td>
<td></td>
</tr>
</tbody>
</table>

The tests for the selected gas compositions were done at 300K, and 373K. The separation experiments for the HighBio product gas compositions were done at 300K, 373K and 473K. The 473K separation experiments were based on the conditions from the HighBio product gas. During the high temperature separation experiments (373K and 473K), the membrane cell was also heated with the electric furnace. However, in the low temperature separation experiments, the membrane cell was heated only using the heating mantle. Figure 26 depicts the process flowsheet for the separation experiments.

![Figure 26. Process flowsheet for the separation of CO₂/N₂ mixtures.](image)

Furthermore, all the investigated feed compositions were tested with ZSM5-I membrane except in the HighBio product gas compositions, CO₂:N₂ (2.8:7.2), which was tested with the ZSM5-II membrane at low temperature (300K). During the high temperature experiments (473K), the temperature rose excessively high that led to the deterioration of the ZSM5-I membrane. Therefore, ZSM5-II was used in the remaining tests. The CO₂:N₂ compositions (1:9 and 1:1), were also tested with the ZSM5-II membrane. These tests were done at low temperature (300K), and the separation performances were compared to those of similar compositions that were done with the ZSM5-I at the same
temperature. In all the separation experiments, the feed and permeate pressures were kept constant at 6 bar and 1 bar respectively. The measurements and reading of the gas flow rates, the temperatures and pressures were done as in the previous sections (sections 5.3 and 5.4). However, in order to minimize errors, the measurements and the samples were taken when the temperature, pressure and the flow rates of the experimental conditions has stabilized in the range of ±0.2, ±0.02 and ± 0.01 respectively. The feed, permeate and retentate samples were taken using the syringe at their respective outlets. The average of the feed, permeate and retentate from the GC analysis of each of the samples were taken. The separation factors of the samples were calculated from Eq. (33).

\[
\alpha = \frac{y_{CO_2}/y_{N_2}}{x_{CO_2}/x_{N_2}},
\]  

(33)

where \( \alpha \) is the separation factor, \( y \) and \( x \) are the average molar fractions at the exit of the permeate, and the retentate respectively. Furthermore, the membrane permeabilities of each of the samples were calculated from Eq. (34).

\[
\hat{P} = \frac{F_x}{A \cdot \Delta p},
\]  

(34)

where \( \hat{P} \) is the permeance of gas \( x \) [mol s\(^{-1}\) m\(^2\) Pa\(^{-1}\)], \( F_x \) is the flow rates of gas \( x \) [mol s\(^{-1}\)], \( A \) is the unit area of membrane [m\(^2\)], and \( \Delta p \) is the partial pressure difference between the feed and the permeate [Pa]. Additionally, the CO\(_2\) permeation fluxes of the samples were calculated from Eq. (35).

\[
J = \frac{F}{A},
\]  

(35)

where \( J \) is the CO\(_2\) permeation flux [kg m\(^{-2}\) h\(^{-1}\)], and \( F \) is the permeate flow rate [kg h\(^{-1}\)].
5.6. Design of zeolite membrane separation process for separating CO$_2$ and N$_2$

The aim of this section is to evaluate a zeolite membrane separation process such that about 98% of the CO$_2$ can be recovered from the previous separation experiment with the feed composition of CO$_2$:N$_2$ (2.8:7.2). Depending on the number of successive membrane modules, the process flowsheet can be depicted as shown in Figure 27 below.

![Flowsheet for the multi-stage zeolite membrane separation process.](image)

**Figure 27.** Flowsheet for the multi-stage zeolite membrane separation process.

For the purpose of this design, the following assumptions were made:

- The flow rate and permeability changes with increasing gas compositions.
- The gas stream has the same composition as the permeated and rejected stream at all points through the membrane.
- There was a negligible pressure drop in feed side.

The process flowsheet in each stage is similar to that of Figure 26. However, the permeate compositions from each stage were compressed to a pressure of 6 bar, which are used as feed in the subsequent stage. The feed temperature of 300K was kept constant in each stage. The initial feed flow rate used was 1 mol s$^{-2}$. The calculations of permeances and permeate compositions as results of increased CO$_2$ compositions in the mixture were done with respective graph equations. The graphs were permeance as function of CO$_2$ permeate compositions, and CO$_2$ permeated as function of CO$_2$ retentate that were obtained in the low temperature separation experiments (see Fig 39-
40). The average of the permeate flow rates obtained in the low temperature separation experiments was used to calculate the respective permeate flow rates in each stage. The corresponding retentate flow rates in each stage are obtained from the overall material balance given by,

\[ F_f = F_p + F_r, \quad (36) \]

where \( F_f, F_p \) and \( F_r \) represent the feed, permeate and retentate flow rates respectively. The retentate compositions in each stage were calculated also from the material balance given by,

\[ F_f y_f = F_p y_p + F_r y_r, \quad (37) \]

where \( y_f, y_p \) and \( y_r \) represent the mole fraction of CO\(_2\) in the feed, permeate and retentate respectively. Hence, the corresponding areas in each stage were calculated by rearranging Eq. 34.
6. Results and Discussion

6.1. Determination of Calibration Curves

The CO₂/N₂ mixtures prepared in the laboratory of different compositions (1:1, 2:3, 3:2, 4:1, 1:4, and 9:1), 100% CO₂ and 100% N₂ were analyzed by the gas chromatograph. The aim was to determine the instrument response with regards to change in the concentrations of the analyzed mixtures. Although the correlation coefficients (R²) values from GC analysis were within the recommended values, however, some of the standard points in linear, quadratic and cubic curves do not pass through the line curves. Alternatively, the obtained data from the GC analysis were compared with the Excel analysis to determine the goodness-of-fit. The comparison was done base on the r-squared values, residual plots and the sum square of the absolute difference between the curves and the data points. Additionally, the comparisons were made with the tests compositions, CO₂:N₂ (1:1, and 9:1). The comparisons of the different models show goodness-of-fit for both CO₂ and N₂ in this study were the cubic-fit (Fig. 28 and 29). The results of the comparisons are presented in Tables 8 and 9 below.

![CO₂ calibration curve](image)

**Figure 28.** CO₂ calibration curve.
Figure 29. N\textsubscript{2} calibration curve.

### Table 8. Comparisons of the models for the CO\textsubscript{2} GC and Excel analyses.

<table>
<thead>
<tr>
<th>Model</th>
<th>R\textsuperscript{2} GC</th>
<th>R\textsuperscript{2}</th>
<th>Residual at 50 % CO\textsubscript{2}</th>
<th>∑ABS (y-f) with 50% CO\textsubscript{2}</th>
<th>Residual at 90% CO\textsubscript{2}</th>
<th>∑ABS (y-f) with 90% CO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>0.99809</td>
<td>0.9753</td>
<td>6318.172</td>
<td>21260.12</td>
<td>4404.59</td>
<td>17258.60</td>
</tr>
<tr>
<td>Quadratic</td>
<td>0.99828</td>
<td>0.9778</td>
<td>20215.46</td>
<td>93285.28</td>
<td>3737.54</td>
<td>18823.20</td>
</tr>
<tr>
<td>Cubic</td>
<td>0.99928</td>
<td>0.9907</td>
<td>3274.041</td>
<td>15166</td>
<td>2522.47</td>
<td>13248.20</td>
</tr>
<tr>
<td>Piecewise</td>
<td>1</td>
<td>1</td>
<td>7182.316</td>
<td>35019.91</td>
<td>5483.865</td>
<td>27875.97</td>
</tr>
</tbody>
</table>

### Table 9. Comparisons of the models for the N\textsubscript{2} GC and Excel analyses.

<table>
<thead>
<tr>
<th>Model</th>
<th>R\textsuperscript{2} GC</th>
<th>R\textsuperscript{2}</th>
<th>Residual at 10% N\textsubscript{2}</th>
<th>∑ABS (y-f) with 10% N\textsubscript{2}</th>
<th>Residual at 50% N\textsubscript{2}</th>
<th>∑ABS (y-f) with 50% N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>0.99681</td>
<td>0.9497</td>
<td>7297.401</td>
<td>28259.6</td>
<td>4244.49</td>
<td>21577.73</td>
</tr>
<tr>
<td>Quadratic</td>
<td>0.99895</td>
<td>0.9835</td>
<td>5086.008</td>
<td>14646.5</td>
<td>5961.699</td>
<td>39895.83</td>
</tr>
<tr>
<td>Cubic</td>
<td>0.99931</td>
<td>0.9891</td>
<td>2898.376</td>
<td>12510.6</td>
<td>713.9429</td>
<td>11118.82</td>
</tr>
<tr>
<td>Piecewise</td>
<td>1</td>
<td>1</td>
<td>5322.551</td>
<td>21381.53</td>
<td>3967.24</td>
<td>45695.47</td>
</tr>
</tbody>
</table>
Although piecewise is naturally best on $R^2$ comparison, cubic was selected due to the comparison with the test compositions of CO$_2$ and N$_2$. The residual plots between the independent variables and the predicted variables, as well as the sum square of the absolute difference between the curves and the data points were smaller in the cubic-feet models compared to the other models. Similarly, the obtained R-squared values from the Excel analysis indicate that the goodness-of fits were cubic.

### 6.2. Separation Factors

Separation factor is one generally used criterion to determine the performance of a membrane in certain separation task. Figures 29 and 30 depict the results of all the feed compositions tested in this study. The results obtained in this study are relatively comparable to the results obtained in the literature (see Table 10).

<table>
<thead>
<tr>
<th>Zeolite Membrane</th>
<th>Temp (K)</th>
<th>Feed CO$_2$:N$_2$</th>
<th>$\alpha$CO$_2$/N$_2$</th>
<th>CO$_2$ Permeance (mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$)</th>
<th>CO$_2$ PF (kg m$^{-2}$ h$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>300</td>
<td>1:1</td>
<td>2.9</td>
<td>$5.3 \times 10^{-8}$</td>
<td>2.1</td>
<td>This work</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>300</td>
<td>2.3:7.7</td>
<td>2.8</td>
<td>$8.3 \times 10^{-8}$</td>
<td>1.8</td>
<td>This work</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>300</td>
<td>1:1</td>
<td>16</td>
<td>$9.8 \times 10^{-7}$</td>
<td>0.7</td>
<td>Poshusta et al. (2000)</td>
</tr>
<tr>
<td>K-Y</td>
<td>313</td>
<td>1:1</td>
<td>30.3</td>
<td>$1.8 \times 10^{-6}$</td>
<td>14.3</td>
<td>Kusakabe et al. (1999)</td>
</tr>
<tr>
<td>NA-Y</td>
<td>303</td>
<td>4:1</td>
<td>5</td>
<td>-</td>
<td>9.1</td>
<td>Clet et al. (2000)</td>
</tr>
<tr>
<td>K-ZSM-5</td>
<td>323</td>
<td>1:1</td>
<td>2</td>
<td>$4.5 \times 10^{-8}$</td>
<td>0.4</td>
<td>Masuda et al. (1998)</td>
</tr>
<tr>
<td>B-ZSM-5</td>
<td>300</td>
<td>6:1</td>
<td>12.6</td>
<td>$2.6 \times 10^{-7}$</td>
<td>5.1</td>
<td>Bernal et al. (2004)</td>
</tr>
</tbody>
</table>

It is noteworthy in Table 10 that the selectivity of the ZSM-5 membrane was in line with the K-ZSM-5 membrane from the literature. In this work, under low temperature (300K), the highest membrane selectivity of 2.9 was achieved at CO$_2$/N$_2$ (1:1) mixture.
The lowest membrane selectivity under this temperature was observed at CO$_2$/N$_2$ (1:9) mixture (see Fig. 30).

Figure 30. Separation factors as function of CO$_2$:N$_2$ feed ratio at 300K and 373K under constant feed pressure of 6 bar and permeate pressure of 1 bar in the separation experiments of the selected gas compositions.

It can be observed from Fig. 30 that the separation factors for the separation experiments of the selected feed compositions decreased from 2.2 to 2.1 with the increased concentration of CO$_2$ in the CO$_2$/N$_2$ mixtures 4:1 and 9:1 respectively. However, under this temperature, a membrane selectivity of 2.8 in CO$_2$/N$_2$ (2.3:7.7) was observed in the separation experiments of the HighBio product gas compositions (Fig. 30). Similarly, at high temperature (373K) for the separation experiments of the selected feed gas compositions, the highest membrane selectivity of 2.16 was observed in CO$_2$/N$_2$ (4:1) mixture, which was slightly higher than with the 1:1 mixture. This could be expected in high temperature separations of the zeolite membranes. The lowest separation factor was however observed in the CO$_2$/N$_2$ (1:9) as it was the case with the low temperature separation experiments. In the separation experiments of the HighBio product gas compositions, the highest separation factor was achieved when the
concentration of CO\textsubscript{2} in the mixture was 23 mol-% (Fig. 31). This was also attained at low temperature.

![Graph](image)

**Figure 31.** Separation factors as function of temperature at constant feed pressure of 6 bar and permeate pressure of 1 bar in the separation experiments of the HighBio product gas compositions.

Similarly, the separation factor of the CO\textsubscript{2}:N\textsubscript{2} (2.8:7.2), which was done with the ZSM5-II at low temperature was slightly higher than the separation factor of the same gas compositions that was done with the ZSM5-I. This could therefore be attributed to the similar properties in both the ZSM-5 membrane materials.

### 6.3. Permeances

Further to separation factors in the determination of membrane separation performances, is the permeance. The membrane permeance is calculated with Eq. (33). In this study, the highest CO\textsubscript{2} permeance of the zeolite membranes was observed when the concentration of the CO\textsubscript{2} in the mixture was 10 mol-\%. This was observed both at low (1.8.10\textsuperscript{-7} mol s\textsuperscript{-1} m\textsuperscript{2} Pa\textsuperscript{-1}) and high (1.71. 10\textsuperscript{-7} mol s\textsuperscript{-1} m\textsuperscript{2} Pa\textsuperscript{-1}) temperature separation experiments of the same gas compositions respectively. For N\textsubscript{2}, the highest membrane permeance was also achieved when the N\textsubscript{2} concentration in the mixture was 10 mol-\%. This was also the case both at low (2.0. 10\textsuperscript{-7} mol s\textsuperscript{-1} m\textsuperscript{2} Pa\textsuperscript{-1}) and high (1.4.
$10^{-7}$ mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$) temperature separation experiments. However, both the CO$_2$ and N$_2$ permeances decreased with the increasing concentrations of the gases both at low and high temperatures. Therefore, the results in this study indicate that higher zeolite membrane permeability can be achieved with a low gas concentration. However, in the HighBio product gas separation experiments, the highest CO$_2$ and N$_2$ permeances were both achieved in the low temperature separation experiments. The lowest CO$_2$ and N$_2$ permeances were however, observed in the high temperature (473K) separation experiments. This further indicates that, the permeability of a gas in the zeolite membranes is favorable at low temperatures.

Furthermore, the comparison of the two membranes in the separations of gas mixtures with similar compositions at low temperature shows that, the ZSM5-I membrane has better CO$_2$ and N$_2$ permeabilities than the ZSM5-II. However, the differences are negligible, which might be a result from the slight variations in the experimental conditions. The results are depicted in Figures 32–33 below.

![Figure 32. CO$_2$ permeances as function of CO$_2$ feed compositions at 300K, 373K and 473K and constant feed and permeate pressures of 6 bar and 1 bar respectively.](image)
6.4. CO$_2$ Permeation Fluxes

Figures 34-35 show the CO$_2$ permeation fluxes through the membrane for both the selected feed and HighBio gas compositions respectively. In the permeate flux analysis, it was observed that, at the low temperature the highest CO$_2$ permeation flux through the membrane was observed when the mole fraction of CO$_2$ in the mixture was 0.9. The permeation fluxes under this temperature decreased as the concentration of CO$_2$ is decreased. In the high temperature separation experiments (373K), the highest CO$_2$ permeation flux of 2.01 kg m$^{-2}$ h$^{-1}$ was achieved in 1:1 mixture. However, the fluxes decreases to 1.95 kg m$^{-2}$ h$^{-1}$ in the separation experiment of CO$_2$/N$_2$ (4:1) mixture, and increases to 2 kg m$^{-2}$ h$^{-1}$ as the CO$_2$ concentration in the mixture was increased to 90 mol-%. This was probably also as result of changes in the CO$_2$ adsorption equilibrium of the membrane at high temperature. On the other hand, the CO$_2$ permeation fluxes decreased as a function of the temperature in the separation experiments performed with the HighBio product gas compositions. This was observed in both the two compositions as well as the ZSM5-II separation experiment done with CO$_2$/N$_2$ (2.8:7.2). However, the highest CO$_2$ permeation flux of 2.14 kg m$^{-2}$ h$^{-1}$ was achieved in the separation experiments of the HighBio product gas compositions. This was observed in the
separation experiment using the ZSM5-II when the CO₂ composition in the mixtures was 28 mol- % and at low temperature.

Moreover, in the comparisons of the two membranes performances with regards to CO₂ permeation fluxes of the same gas compositions, ZSM5-II possesses a better CO₂ flux at CO₂/N₂ (1:1) than ZSM5-I. On the other hand, the ZSM5-I membrane shows a better CO₂ flux at CO₂/N₂ (1:9) than ZSM5-II. However, both membranes show an impressive CO₂ fluxes compared to some of the results reported in the literatures (see Table 10). In addition to that, the relative CO₂ permeation flux of the single gas of the ZSM5-I at low temperature and same constant feed and permeate pressures was 3.1 kg m⁻² h⁻¹. Therefore, it can be said that both membranes performances were fairly impressive.

\[ \text{Figure 34. CO₂ permeation fluxes as function of CO₂ feed composition of the ZSM5-I at 300K, 373K and ZSM5-II at 300K under constant feed pressure of 6 bar and permeate pressure of 1bar in the separation experiments of the selected gas compositions.} \]
Figure 3. CO₂ permeation fluxes as function of temperature and constant feed pressure of 6 bar and permeate pressure of 1 bar in the separation experiments of the HighBio product gas compositions.

6.5. Influence of Pressure and Temperature

Figure 36-38 depict the permeate flow rates as a function of the feed pressure. The experiments were done to determine the influence of pressure in the separation of CO₂/N₂ mixtures using the ZSM5-I membrane. At both low and high temperatures, the permeate flow rates increases with increasing pressure. This indicates that the pressure has significant influence on permeate flows. However, the permeate flow rates were higher at the low temperature (300K) compared to similar compositions at high temperature. Hence, the permeate flow rates have a significant influence on the membrane permeability and CO₂ permeation flux. As was earlier observed in the permeance and permeation flux experiments, under low temperature, the highest CO₂ permeation flux was achieved with CO₂/N₂ (9:1) mixture. This corresponds to 0.3742 nl min⁻¹, which was the highest permeate flow rate comparing all the feed compositions and process conditions. Table 11 shows the permeate flow rates, temperatures, CO₂ permeation fluxes and permeances obtained in this study.
Table 11. Permeate flow rates, temperatures, CO₂ permeation fluxes and permeances obtained in this study.

<table>
<thead>
<tr>
<th>Samples (CO₂:N₂)</th>
<th>Temp. (K)</th>
<th>Permeate flow rates (nl min⁻¹)</th>
<th>CO₂ permeation fluxes (kg m⁻² h⁻¹)</th>
<th>Permeances (10⁻⁸ mol s⁻¹ m⁻² Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>1:1</td>
<td>300</td>
<td>0.3343</td>
<td>2.090268288</td>
<td>5.32646</td>
</tr>
<tr>
<td>4:1</td>
<td>300</td>
<td>0.3551</td>
<td>2.220268288</td>
<td>3.6643</td>
</tr>
<tr>
<td>9:1</td>
<td>300</td>
<td>0.3742</td>
<td>2.339691336</td>
<td>3.364</td>
</tr>
<tr>
<td>1:9</td>
<td>300</td>
<td>0.2819</td>
<td>1.762584146</td>
<td>18.0107</td>
</tr>
<tr>
<td>1:1</td>
<td>373</td>
<td>0.3218</td>
<td>2.012059527</td>
<td>5.17974</td>
</tr>
<tr>
<td>4:1</td>
<td>373</td>
<td>0.3116</td>
<td>1.9482831257</td>
<td>3.13879</td>
</tr>
<tr>
<td>9:1</td>
<td>373</td>
<td>0.3205</td>
<td>2.003931257</td>
<td>2.98225</td>
</tr>
<tr>
<td>1:9</td>
<td>373</td>
<td>0.2813</td>
<td>1.758832644</td>
<td>17.1054</td>
</tr>
</tbody>
</table>

It can be observed from Table 11 that, the permeate flow rates decreased with decreasing CO₂ compositions at low temperature. On the other hand, at high temperature, the permeate flows rates decreased with increasing concentration of CO₂ from 50 mol-% to 90 mol-%, before it decreased in ascending order at CO₂ concentration of 40 mol-% and 10 mol-%. This could be further attributed to the changes in the CO₂/N₂ adsorption equilibrium of the membrane at high temperature. The trends were similar in the CO₂ permeates fluxes and permeances in all the feed compositions tested in this study.
Figure 36. CO$_2$ permeance of the single gas component as function of different feed pressures and constant permeate pressure of 100 kPa at 300K and 373K.

Figure 37: N$_2$ permeance of the single gas component as function of different feed pressures and constant permeate pressure of 100kPa at 300K and 373K.
Figure 38. CO\textsubscript{2} permeation fluxes of the single gas component as function of different feed pressures and constant permeate pressure of 100kPa at 300K and 373K.

6.6. Evaluation of the Multi-stage Process Design

As was observed in this study, a single stage membrane system is beneficial only for a moderate CO\textsubscript{2} purity and a recovery. Hence, a multi stage membrane system is essential for a higher purity and better CO\textsubscript{2} recovery (Qi and Henson 1998). The results of the evaluation are shown in Table 12 and Figure 39-40 below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
<th>Stage 5</th>
<th>Stage 6</th>
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<tbody>
<tr>
<td>Mole fraction of CO\textsubscript{2} feed</td>
<td>0.28</td>
<td>0.5015</td>
<td>0.7519</td>
<td>0.8928</td>
<td>0.94685</td>
<td>0.9721</td>
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<tr>
<td>Mole fraction of CO\textsubscript{2} permeated</td>
<td>0.5015</td>
<td>0.7519</td>
<td>0.8928</td>
<td>0.94685</td>
<td>0.9721</td>
<td>0.9859</td>
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<tr>
<td>Mole fraction of CO\textsubscript{2} retentate</td>
<td>0.2504</td>
<td>0.4681</td>
<td>0.7331</td>
<td>0.8856</td>
<td>0.9435</td>
<td>0.9703</td>
</tr>
<tr>
<td>Permeate flow rate (mol s\textsuperscript{-1})</td>
<td>0.0117841</td>
<td>0.0138866</td>
<td>0.0016364</td>
<td>0.0001928</td>
<td>2.272E-05</td>
<td>2.677E-06</td>
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<tr>
<td>Retentate flow rate (mol s\textsuperscript{-1})</td>
<td>0.8821586</td>
<td>0.1039548</td>
<td>0.0122502</td>
<td>0.0014436</td>
<td>0.0001701</td>
<td>2.014E-05</td>
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<tr>
<td>Area (m\textsuperscript{2})</td>
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<td>0.84398</td>
<td>0.09465</td>
<td>0.01095</td>
<td>0.001285</td>
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<td>Partial pressure difference (Pa)</td>
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<td>225725.88</td>
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<td>441016.64</td>
<td>470895.44</td>
<td>484675.38</td>
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<tr>
<td>Permeability (mol s\textsuperscript{-1} m\textsuperscript{-2} Pa\textsuperscript{-1})</td>
<td>1.339E-07</td>
<td>7.289E-08</td>
<td>4.778E-08</td>
<td>3.994E-08</td>
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<tr>
<td>Total no of required modules</td>
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<td></td>
<td></td>
<td>6</td>
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</table>
Figure 39. CO₂ permeance as function of CO₂ permeate at 300K and constant feed pressure of 6 bar and constant permeate pressure of 1 bar with CO₂:N₂ (2.8:7.2) feed mixture using multi-stage ZSM5 membrane modules.

Figure 40. CO₂ permeate as function of CO₂ retentate at 300K and constant feed pressure of 6 bar and constant permeate pressure of 1 bar with CO₂:N₂ (2.8:7.2) feed mixture using multi-stage ZSM-5 membrane modules.
Based on the given conditions, it can be observed from Fig. 39-40 that high CO\textsubscript{2} recovery in the permeate side can be achieved with the multi-stage membrane modules. This can be achieved with a total membrane surface area of 8.419966 m\textsuperscript{2} of the 6 membrane modules. However, in the last stage the CO\textsubscript{2} permeate composition of 0.9859 was obtained. Therefore, for high purity of CO\textsubscript{2} in the separation experiment of CO\textsubscript{2}:N\textsubscript{2} (2.8:7.2) mixture with the ZSM-5 used in this study, and at 300K and constant feed pressure of 6 bar and constant permeate pressure of 1 bar, 6 successive membrane modules can be employed.

### 6.7. Evaluation of the Experimental Errors

In a laboratory experiment, errors can be encountered for instance as induced by an analyzer. However, these errors can be evaluated by relative percent error or standard deviation analyses. Figure 41-42 depicts the evaluation of experimental errors from this study. However, all the feed measurement percent errors were below 10%. The only exception been in the separation experiments where each of the gas composition in the mixtures were 10 mol. %, as well as in the high temperature separation experiment with 23 mol. % CO\textsubscript{2} in the mixture. The comprehensive lists of the evaluation of the experimental errors from this study are presented in the appendices of this report.

![Figure 41](image.png)

**Figure 41.** CO\textsubscript{2} percent error as function of CO\textsubscript{2} composition in the feed mixture at low (300K) and high (373K0) separation experiments.
Figure 42. N2 percent error as function of N2 composition in the feed mixture at low (300K) and high (373K) separation experiments.
7. Conclusions

The aim of this study was to evaluate the possible applications of the biomass-derived syngas, as a follow up to the earlier biomass gasification research of the HighBio project. The bio-syngas is usually produced with gasification process, which is considered as one of the most attractive conversion technologies, due to the several industrial applications of the derived syngas.

Biomass-derived syngas offers carbon neutral fuels compared to syngas from fossil fuels sources. The syngas from gasification process is generally produced in a gasifier. The different types of gasifiers for biomass gasification include updraft, downdraft, crossdraft, entrained-flow and plasma gasifiers. The choice of a gasifier for the gasification process depends on the feedstock and its properties, the desired gas quality and capacity requirement. The syngas from biomass gasification process can be utilized in the generation of power, heat, fuels and chemicals. The promising applications of the derived syngas are in the production of transportation fuels via Fischer-Tropsch, methanol and mixed alcohols syntheses, production of chemicals such as hydrogen production, and ammonia synthesis.

In any of these applications, a high degree of treatment and condition of the syngas is required. The treatment is usually carried out to remove undesirable impurities, while the conditioning of the gas is done to get the right H\textsubscript{2} to CO ratio. The treatment and conditioning of syngas are generally done, in order to meet the downstream process requirement in relation to size and cost. However, CO\textsubscript{2} is one of the major by-products in gasification process. The removal of CO\textsubscript{2} is desirable in order to reduce the CO\textsubscript{2} emissions or to meet the downstream process requirements. Absorption processes are the most developed techniques in the separation of CO\textsubscript{2} in the industries. However, other techniques that are recently gaining interests are adsorption, membrane separation, cryogenic fractionation, hydrate based separations, chemical-looping combustion and enzyme based separation.

Moreover, two MFI-types zeolite membranes (ZSM5-I and ZSM5-II) were tested in the separation of CO\textsubscript{2} from CO\textsubscript{2}/N\textsubscript{2} mixtures in a laboratory scale experiments. Separation factor, gas permeability and CO\textsubscript{2} permeate flux were the parameters used to determine the membrane performance. The highest membrane performances of the feed gas
compositions were achieved with low CO$_2$ gas composition, and at the low temperature separation experiments.

However, in this study high CO$_2$ recovery was not achieved with the single stage separation with the ZSM5 zeolite membranes. Hence in order to achieve high recovery and purity of CO$_2$, the separation experiment of the HighBio CO$_2$/N$_2$ feed composition using the ZSM5 zeolite membrane was evaluated at low temperature and constant feed and permeate pressures of 6 bar and 1 bar respectively. Based on the analysis, it is suggested that 6 successive membrane modules should be employed. Further investigations that incorporate other product gas compositions from biomass gasification, as well as the study of other type of inorganic membranes more suitable to CO$_2$/N$_2$ separation processes are highly recommended. The economic analysis of the multi-stage ZSM5 zeolite membrane separation could be also another interesting study.
References


## Appendix A

### Table 13. \( \text{CO}_2 \) feed measurement errors

<table>
<thead>
<tr>
<th>( \text{CO}_2 ) in the feed (( \text{CO}_2: \text{N}_2 ))</th>
<th>Temperature (K)</th>
<th>Measured value (mol. %)</th>
<th>Error (%)</th>
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<td>10</td>
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<td>300</td>
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<td>300</td>
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<td>373</td>
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<td>373</td>
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<td>88.76279</td>
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### Appendix B

#### Table 14. \( \text{N}_2 \) feed measurement errors

<table>
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<tr>
<th>( \text{N}_2 ) in the feed (CO(_2):( \text{N}_2 ))</th>
<th>Temperature (K)</th>
<th>Measured value (mol. %(^1))</th>
<th>Error (%)</th>
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<td>373</td>
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<td>373</td>
<td>87.24482333</td>
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</table>
### Table 15. CO₂ Deviation of the chromatography analysis

<table>
<thead>
<tr>
<th>CO₂ Composition in CO₂:N₂ (mol. %)</th>
<th>Temp. (K)</th>
<th>Measured composition (mol. %)</th>
<th>Mean µ (mol. %)</th>
<th>Deviation σ (mol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>300</td>
<td>x₁: 12.02713, x₂: 11.98979, x₃: 11.98353</td>
<td>12.00015</td>
<td>0.019248</td>
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<tr>
<td>50</td>
<td>300</td>
<td>x₁: 51.02696, x₂: 51.04385, x₃: 50.76896</td>
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<td>300</td>
<td>x₁: 82.00792, x₂: 82.17392, x₃: 81.59871</td>
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<td>90</td>
<td>300</td>
<td>x₁: 87.60782, x₂: 87.54302, x₃: 87.38543</td>
<td>87.51209</td>
<td>0.093387</td>
</tr>
<tr>
<td>10</td>
<td>373</td>
<td>x₁: 12.29335, x₂: 12.21012, x₃: 12.14132</td>
<td>12.21493</td>
<td>0.062159</td>
</tr>
<tr>
<td>50</td>
<td>373</td>
<td>x₁: 50.79307, x₂: 50.23574, x₃: 50.03575</td>
<td>50.35485</td>
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<td>x₁: 82.07576, x₂: 81.88241, x₃: 81.64229</td>
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<td>x₁: 88.99132, x₂: 88.82368, x₃: 88.47337</td>
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## Table 16. N₂ Deviation of the chromatography analysis

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<tr>
<th>N₂ Composition in CO₂:N₂ (mol. %)</th>
<th>Temp. (K)</th>
<th>Measured composition (mol. %)</th>
<th>Mean μ (mol. %)</th>
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<th>N₂ Composition in CO₂:N₂ (mol. %)</th>
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