The potential of petro-/chemical sectors for industrial decarbonization – Part I

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Summary

Facing energy transition and carbon mitigation is the subject of different sectors from energy production and industries to the transportation and building constructions. This study focuses on the industrial decarbonization and investigates carbon dioxide (CO_2) emission from different petro-/chemical plants. For this research project, the emission rate and CO_2 stream purity of various petro-/chemical sub-sectors were listed to find the low hanging fruit options towards decarbonization. Then, the processes are categorized and described, deriving the most important parameters from different literatures to generate an essential dataset for each product. This paper includes main achievements over ethylene-oxide and ammonia production and investigates the CO_2 emission sources at the related processes, it also introduces novel decarbonization approaches.

Introduction

A considerable part of the fossil CO_2 emissions comes from the industrial sector with a share of 23% [1]. Overall, the industrial sector is the second carbon emitter after energy production. In the framework of energy transition for Belgium, decarbonization of industries is important to reach carbon-neutrality by 2050. Between the energy intensive industrial sectors, the petro-/chemical plants are more complicated due to the presence of carbon not only in fuels but also, in feedstocks and products. Therefore, this basic research aims on the possibility of carbon mitigation at petro-/chemical sectors by providing a hierarchy of plants based on their emission and providing a schematic overview on the processes and related CO_2 emissions. Based on the primary research study, the purity of the emitted CO_2 is important for the initial steps of carbon capture strategies. Hence, this study explores the ethylene-oxide and ammonia production plants and provides details on the essential parameters of these processes. Furthermore, this paper releases the main part of study up to now and the dataset is going to be extended further in the next steps of the research.

Technologies and project description

Ethylene oxide (EO) is extremely reactive and considered one the most versatile chemical intermediates. EO is utilized directly as sterilizer or disinfectant, however, in most cases EO is further processed to produce a wide spectrum of products. Ethylene glycols (mono-, di-, triethylene glycol) is the largest final products of the EO processing with the share of 73% of the EO market in 2018. Other dominant end uses are converting of EO to the higher-value derivatives such as ethoxylate, ethanolamine, glycol ethers, polyethylene glycol, polyether polyols, surfactants and glycol ethers [2], [3], [4]. For EO production within the Europe, Germany is forecast to grow at approximately 3.2% CAGR (Compound Annual Growth Rate) over the 2020-2027 period [5]. EO production lines in Belgium are BASF and Ineos plants located in Antwerp with capacity of 500,000 ton/year and 420,000 ton/year respectively at 2013 [6]. These two plants have announced to extend their production resulting in the whole EO production capacity of Belgium to more than 1,320,000 ton/year [7], [8]. EO is one of the key chemical products through Europe. The share of EO manufacturing for 15 top plants by capacity in Europe and the year 2013 are listed in table 1.

Table 1. European EO capacity at EU countries in 2013 [6]

Company	Capacity (kt/y)
Germany	1090
Belgium	920
Russia	614
Netherlands	470
France	250
Spain	135
Poland	115
Sweden	100

The basic materials for EO production are high-purity grade oxygen and ethylene. The direct oxidation of ethylene, can be air-based or oxygen-based and the general process scheme is depicted in Figure 1. In Flanders, one of the EO production sites has installed the CO_2 capture facilities and a rough estimates shows possibility of 2.5 Mt CO_2 mitigation from high carbon concentration plants [9].

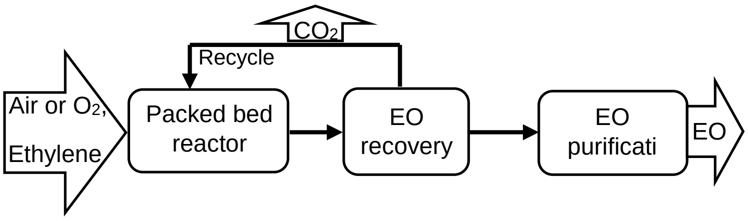

Figure 1. Block flow diagram of a conventional oxidation process for the EO production [10]

Ammonia production is investigated as the second CO_2 emitting plant. Ammonia is critical in the manufacturing of fertilizers, and is one of the largest-volume synthetic inorganic chemicals produced worldwide [11], [12]. Moreover, ammonia is an ideal carbon-free energy carrier and storage material [13], [14]. Capacity of ammonia production through the European countries and number of plants per country are listed for the year 2013 [15]. Ammonia production releases about 1.3 ton process related CO_2 and 0.6 ton CO_2 emissions related to combustion. However, estimates show that 100% of the high CO_2 concentration process emissions which stands for 70% of the total emissions can be captured

Table 2. Production capacity of ammonia at EU countries in 2013 [15]

Countries	Capacity (kt)
Germany	3,438
Poland	3,210
Netherlands	2,717
Romania	2,176
France	1,495
Lithuania	1,118
Bulgaria	1,118
UK	1,100
Belgium	1,020
Spain	609
Italy	600
Austria	485
Slovakia	429
Hungary	383
Czech Rep.	350
Estonia	200
Greece	165
Total EU-27	20,613

The main industrial procedure for the production of ammonia is artificial nitrogen fixation called Haber–Bosch process. In this process, nitrogen (N_2) reacts with hydrogen (H_2) both at gaseous statues under high pressures of 150 to 200 bar and temperature 500 °C. The overall reaction is $N_2 + 3H_2O \rightarrow 2NH_3 + 3/2O_2$ [16], [17]. Feedstock for the Haber process are air and natural gas to supply N_2 and H_2 respectively. The other raw materials are coal and naphtha which release more than double greenhouse gases (GHGs) in comparison to natural gas [16]. Figure 2 depicts the ammonia production plant utilizing natural gas as feedstock. Novel electric assisted technologies such as direct electrochemical ammonia synthesis and solid oxide electrolyzers are, also, under development [18].

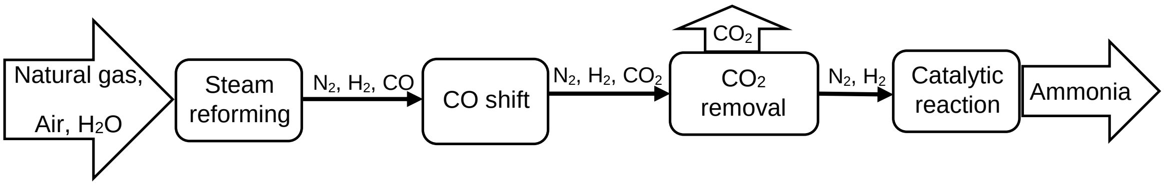

Figure 2. Main schematic sub-processes of ammonia synthesis via Haber–Bosch process [19]

Cost and energy briefs

1- EO

As for the energy requirements of EO, the warmth from the exothermic reaction during partial oxidation of ethylene, generates steam on the reactor shell, and is used for heating functions all through the method. Therefore, except the possible start-up requirements, no fuel burning is required.

As for the cost of EO production, the whole working value estimated to supply EO is about $€_{2015}577.2/t_{EO}$. The evaluation was primarily based on a plant constructed within the U.S. with capability to supply 550,000 metric tons per 12 months of EO [20].

2- Ammonia

The minimum energy requirement for the Haber-Bosch process, defined as the heat of combustion of ammonia, is 18.6 GJ/t_{NH3} based on the lower heating value of ammonia.

The price of ammonia is closely related to the price of the feedstock [21]. According to gross estimations, approximately 2/3 of consumed natural gas is used as a feedstock, while around 1/3 is used for energy purposes, and, it makes up approximately 70-85% of the ammonia production costs [22]. Haber–Bosch production cost is the cost of the feedstock and the energy consumed, that is, 80.36 €$_{2019}$/t for natural gas and 199.11 €$_{2019}$/t for hydrogen by water electrolysis [23]. Capital investment for conventional Haber–Bosch facilities are essentially equivalent at 276.11 M€$_{2017}$ for 2000 $t_{Ammonia}$/d [21]. Grundt et al. estimated capital expenses of 176.99 M€$_{2017}$ for a 1000 $t_{Ammonia}$/d facility [21].

Carbon capture storage

Carbon capture storage (CCS) offers viable opportunities in the two EO plants in the Dutch industry abating ~0.1 Mt CO_2 [24]. For these EO plants the CO_2 concentration in flue gas is predicted to be 100% in 2025 and 2040. The estimated electricity requirements (incl. compression) is 0.4 $GJ_e/t_{CO2\ captured}$ for the same years [24].

As for the ammonia production, a modern, optimized and highly efficient methane-fed Haber-Bosch process emits 1.5–1.6 $t_{CO2\text{-}eq}/t_{NH3}$ making the global manufacturing of ammonia accounting for 1.2% of anthropogenic CO_2 emissions[1] [25].

Many of the processes use similar technologies to separate the CO_2 from the gas mixtures, including [26]:

- Membrane separation;
- Chemical solvents, including amine-based solutions (e.g. MEA and MDEA) and hot potassium carbonate based processes (e.g. the Benfield™ process);
- Physical sorbent based process to remove CO_2 from gas mixtures (e.g. SelexolTM, Rectisol);
- Pressure swing adsorption (PSA); and,
- Cryogenic separation processes.

Selection of the appropriate process is dependent on a number of factors including end use specification, gas inlet pressure, cost, size, weight and maintenance needs.

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[1] This value would further increase if $CO_{2\text{-}eq}$ emissions associated to the extraction and transport of natural gas are included

Innovative aspects

A novel route employing supersonic separator (SS) to prevent EO losses. SS route can reduce oxide losses by 83.33 kg/h. This loss reduction leads to +0.9% greater EO production and 95% less EO losses. Consequently, the net value for 20 operation years is 2.5% higher despite 0.11% higher investment costs [27].

As for the ammonia production, electrification of the process is an innovative way to diminish fossil CO_2 emission. However, the electrification of ammonia production process relies on the use of renewable energy and requires considerable amounts of affordable green resources. Switching the hydrogen production method from methane to hydropower-electrolysis reduces the CO_2 emissions from 1.5 to 0.38 $t_{CO2\text{-}eq}/t_{NH3}$ (75% decrease). 76% of the methane consumed in the process is associated with the production of hydrogen via the steam methane reforming (SMR) reaction and the remaining 24% of the methane is consumed as fuel to provide heat of reaction for the endothermic reforming reaction and to raise the necessary process steam [25].

On the other side, ammonia is an interesting candidate for the energy storage. The ammonia molecules can transport electrical energy and improve resilience of the green electricity grid systems [25]. This feasibility of ammonia as an ideal carbon-free energy storage material is due to its high energy density (4.32 kWh/L), high weight fraction of hydrogen (17.65%) and ease of liquefaction under mild conditions [13].

As a practical case, Ola Osman et. Al. have optimized the design of an industrial-scale ammonia plant (1840 Mt/day) that utilizes 100% renewable energy. They concluded that electrolysis was the most energy intensive part of the process with the energy consumption rate of 10.43 kWh/kg_{NH3} considering the electric efficiency of 37.4% [28]**.**

In addition, ammonia can be produced via the biomass-to-ammonia production pathway with inputs of N_2 from air and H_2 from gasification of biomass. The proportion of land area required for highly productive biomass species is only a small fraction between 1 to 5% of the grower's acreage. Therefore, a small investment in land for a bioenergy crop could produce the ammonia for the remaining 95% of acreage [29].

Conclusions

This study summarizes process requirements of two petro-/chemical plants with the highest purity of CO_2 emission. The main sub-processes and CO_2 emission sections are determined.

Then, the cost and energy analysis are gathered. At the end the innovative technologies and approaches toward the carbon mitigation for these processes are discussed. The results summarize that EO production process is exothermic, hence, it is not the subject of electrification with renewable resources. Nonetheless it is a good candidate for CC due to his high CO_2 emissions purity. However, the ammonia production can be fully electrified with green electrification in the energy consumption rate of approximately 10.43 kWh/kg_{NH3} for an industrial-scale ammonia plant of 1840 Mt/day.

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