

CO₂ utilization through integration of post-combustion carbon capture process with Fischer-Tropsch gas-to-liquid (GTL) processes



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ABSTRACT

Carbon capture is addressed as a medium term solution while industry and society are in their path towards future clean energies. However, in the absence of demand market and a revenue source for the recovered almost-pure CO₂, the remained option, i.e. storage, does not seem to justify the economic feasibility of this climate change mitigation approach.

In our current integration study, we consider existence of a Fischer-Tropsch Gas-to-liquid (GTL) plant in the vicinity of a fossil-fuel based power plant. The captured CO₂ with post-combustion carbon capture technologies is fed into the GTL plants' reformer, i.e. a steam reformer or an auto-thermal reformer. We have presented a few case-studies based on optimal process simulation in Aspen Hysys software package. Unlike most of the studies, our objective is to maximize the wax production rate as upgrading could be carried out at demand market side. The results for a 300 MW coal-fired plant, and a GTL plant with the capacity of one train of Sasol Oryx GTL plant in Qatar show that an auto-thermal reformer (ATR) based GTL process does not have flexibility for CO₂ intake, while all of the captured CO₂ fed into the steam-methane reformer (SMR) process could be consumed. In summary, one train of Sasol Oryx GTL plant with a SMR reactor can utilize a net quantity of 105.5 tonnes-CO₂/h with subtracting the purged CO₂. The paper provides a detailed optimization-based data.

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1. Introduction

1.1. Carbon capture and storage

Fossil fuels account for around 87% of the anthropogenic CO₂ emissions [1] and they are argued to be a major contributor to global warming. The main options for shifting from fossil fuels and thus reducing carbon emissions are: (1) reduction of energy consumption, e.g. via efficiency improvement, (2) replacing fossil fuels by cleaner resources such as renewables, and (3) capture and storage of CO₂ [2]. Although the best alternative route to solving the carbon emissions problem would be to use renewable energy sources, most of these energy sources are not currently

competitive with fossil fuels in terms of cost and maturity. As such, fossil fuels will seemingly continue to be relied on at least over the next few decades. Carbon capture and storage (CCS) is therefore viewed as a medium-term solution and a bridge from the current fossil fuel-based energy system to one that has near-zero carbon emissions. For obvious reasons, the main interest in implementation of CCS projects is the large CO₂-emitting sources. It has been shown that power plants account for about 78% of worldwide large stationary CO₂ sources where the other large CO₂ emitting industries are Cement (7%), refineries (6%) and Iron and steel (5%) [3]. Hence, power plants are the main focus in implementation of CCS projects.

There are three approaches for carbon capture including pre-combustion, oxy-fuel and post-combustion, a summary of which could be found elsewhere [4]. Post-combustion carbon capture (PCC) method is based on removing the generated CO₂ from a power plant's effluent, i.e. flue gas stream. Therefore, it requires minimum modifications to existing, and generally old, processes (see schematic of Fig. 1). This positions PCC technology of the

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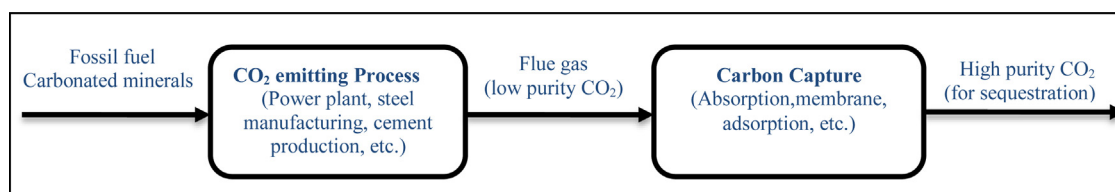


Fig. 1. Schematic of CO₂ emitting process with PCC facility.

highest techno-economic interest amongst the three approaches [5]. In fact, the proposal of PCC started in the 1970s [6] not with the concern for its global warming effect, but as a potential economic source of CO₂, mainly for enhanced oil recovery (EOR) operations. For this reason, PCC is ready today while pre-combustion and oxyfuel methods are still in development phase. Therefore, given the PCC's minimum change requirement to existing power plants and its commercial readiness, this technology may be the most accessible option for retrofitting existing coal plants, while oxyfuel and pre-combustion technologies are studied extensively to be applied into new-build plants [7].

There have been also numerous technologies for PCC, namely solvent-based absorption-desorption [8], membrane [9], adsorption [10] and mineralization [11,12]. Among these, solvent technologies seem to be the most reliable in the medium term as other technologies are still in development phase. Post-combustion carbon capture from flue gas using solvent technology is well understood and is currently used in different industrial applications [13].

The drawback of retrofitting power plants with solvent-based PCC processes is the significant energy penalty introduced which can be in the range of 10–40% of total electricity produced [3]. This notably increases the cost of carbon capture. Another issue is the product of the PCC process. The final product of PCC is almost-pure CO₂. With the existence of very limited demand market for CO₂ consumption as feed stock (e.g. in food industry, enhanced oil recovery, etc.), the remained option is generally the storage of the captured CO₂ underground or beneath the oceans. As such the captured CO₂ is considered as a hassle which needs to be compressed and sent hundreds of kilometers away for sequestration underground or beneath oceans. This further increases the overall costs of carbon capture and puts this options as one of the least wanted approaches for climate change mitigation. Therefore, if carbon capture is to succeed, much more research is needed to find innovative methods to make significant reductions in the capture process and also finding approaches to utilize the captured CO₂ in order to ultimately reduce the overall CO₂ mitigation costs.

CO₂ utilization for production of valuable goods has been addressed in the literature. A combination of steam methane reforming and dry reforming of methane was studied to utilize CO₂ as raw material [14]. The results revealed that net CO₂ emission of the process with combined reformers was reduced by 67% compared to the reference case with a steam reformer. Yagi et al. [15] developed a process and catalyst for CO₂ reforming and production of synthesis gas from a feed gas with low CO₂/carbon and steam to carbon ratios. In another study, the feasibility of chemical looping dry reforming was investigated through thermodynamic screening calculations [16]. The results indicated the possibility of high CO₂ conversion. The direct and indirect synthesis of DME along with CO₂ utilization was performed thermodynamically by Chen et al. [17]. The effect of reaction temperature, H₂/CO and CO₂/CO molar ratios on methanol and DME formation was investigated. It was found that the increase of CO₂/CO molar ratio alleviates the conversion of CO and CO₂ but increases the total consumption of CO₂. In another work by Dixon et al. [18], urea production from CO₂ was modeled and evaluated

based on process efficiency, amount of utilized CO₂, utility requirements, and investment cost. The amount of CO₂ emissions was reported as 0.6 tCO₂ per tCO₂ utilized. Kralj and Glavič [19] studied CO₂ utilization for production of methanol with co-production of electricity from an open gas turbine. Optimization of the process using nonlinear programming yielded an increased annual profit. Techno-economic analysis of a catalytic methanol plant based on renewable energy sources was performed by Clausen et al. [20]. The synthesis gas was produced by combination of set of processes; electrolysis of water, biomass gasification, CO₂ from post-combustion capture and auto-thermal reforming of biogas or natural gas. Hydrogenation of CO and CO₂ to light olefins was studied by Hu et al. over supported iron nano-catalysts [21]. The conversion of CO and CO₂ were reported as 87% and 45%, respectively. Techno-economic and life cycle assessment (LCA) of a biorefinery in which the captured CO₂ during biomass pyrolysis and upgrading is utilized for microalgae production is studied by Sharifzadeh et al. [22]. Capture and utilization of high concentration of CO₂ from the atmosphere to produce a series of carbonates was presented in [23]. The CO₂ utilization methods were bio-butanol and green polymer to utilize nearly 5.55 million tonnes of CO₂ per year. The possibility of CO₂ utilization in water mixtures and fly ash from Polish power plants in underground mines was studied by Uliasz-bochenzyk and coworkers [24,25]. Rafiee and Hillestad investigated the effect of adding CO₂ to a staged FT reactor with iron-based catalyst in order to reduce H₂/CO inside the reactor [26]. The reactor temperature was constrained by 250 °C. Optimizing the FT reactor path with the CO₂ extra feed showed that adding CO₂ had no effect on reducing H₂/CO inside the reactor which was due to the low temperature of the FT reactor. The extra CO₂ extra feed could not reduce H₂/CO by the reverse water gas shift reaction. As an industrial example, Fanavaran petrochemical plant produces one million tonnes of methanol per year through CO₂ utilization. The plant receives natural gas and CO₂ with flowrates of 610,000 tonnes/year and 268,000 tonnes, respectively, from Razi and Marun petrochemical complexes. The imported natural gas and CO₂ together with onsite generated steam are fed to the steam-methane reformer (SMR) and it is fed to the methanol reactor after pressurization [27]. In summary, any form of practical CO₂ utilization pathway would positively impact the feasibility of CCS based climate change mitigation options. The industrial use of captured CO₂ not only can reduce/omit the transportation and sequestration costs, but also opens some revenue streams by selling the CO₂. This arrangement could open notable market for the CO₂ captured from power plants or other CO₂ emitting industries with mutual economic benefits for both CO₂ emitters and CO₂ users. In this paper, we discuss an integration study of PCC process with a Fischer Tropsch Gas-to-liquid (GTL) technology.

1.2. Gas-to-liquid (GTL) technology

Liquid fuels have been always the most favorable fuels compared with gas and solid forms due to their ease of transportation and high energy intensity at the same time. For this reason, there have been extensive efforts, for over a century, to

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